SOILS

THEIR PHYSICS and CHEMISTRY

by

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with a Foreword by

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To

my beloved daughter

TARA

for her genius that made possible the continuation of my researches to the point of this publication.

FOREWORD

The author of this book, Amar Nath Puri, was born in Kasur, Punjab, India, in what is now Pakistan. He was graduated from the government college at Lahore in 1918 and received his M.Sc. there in 1920, winning the Maclagnan gold medal given to the man who stood first among all the science graduates.

In 1921, he went to the Rothamsted Experimental Station at Harpenden, near London, where he was engaged in studies under the direction of B. A. Keen on physico-chemical properties relating to soil colloids. For this work, he was awarded the Ph.D. degree by the University of London in 1924.

On his return to India, the author was successively soil physicist to the government of Punjab, physical chemist to the government of India at the Imperial Research Institute at Pusa, on special duty with the Imperial Council of Agricultural Research of India, physical chemist and head of the chemistry department at the Irrigation Research Station at Lahore, director of the University Institute of Chemistry at Lahore, and founder and director of the Field Research Station Trust at Lahore. In 1929, he was awarded the D.Sc. degree from the University of London.

During the course of these various activities, the author has written, individually and jointly, more than 100 technical papers. These were published in such diverse journals as Annals of Botany, Proceedings of the Royal Society, Journal of Agricultural Science, Journal of the Chemical Society, Journal of the Royal Meteorological Society, Agricultural Journal of India, Memoirs of the Department of Agriculture of India, Imperial Institute of Agricultural Research, Soil Science, Publications of the Irrigation Research Institute, Proceedings of the Lahore Philosophical Society, Indian Concrete Journal, and Journal of the Indian Chemical Society.

These papers present new methods for measuring exchange bases and lime requirements of soils, estimating the gypsum requirements of alkali soils, preventing seepage losses, overcoming damage due to salt efflorescence, avoiding soil deterioration in irrigated areas, improving saline waters for irrigation, stabilizing soil for earth roads, and storing food grains in rural areas.

Other papers deal with such inventions as a siltometer, a chainohydrometer, a salinometer, an apparatus for testing rind-hardness of sugar cane, another for measuring soil shrinkage, a manometric

device for mechanical analysis of soils, a soil-cohesion meter, a soil-erosion meter, and a meter for testing the hardness of soils.

With this as a background, the reader is prepared to consider the author's point of view on the subject with which this book is concerned. The concepts that are contained in it are based in large part on the author's own work, covering a quarter of a century. He starts with the very simple principle of acid-base equilibrium and then proceeds to a consideration of the many highly complicated phenomena that are associated with the colloidal matter in soils. It is important to keep in mind that the author is well trained in classical chemistry.

The book is divided into three parts: the chemistry of the soil, mechanical analysis of soils, and soil moisture. This division highlights the physico-chemical aspects of soils around which some of the most important controversies have developed during the last half century. The author has made no attempt to review the various theories of the several controversialists, because of his belief that these merely serve to confuse the novice and tax the mentality of even the more advanced student.

The history of soil science is a record of ever-changing fashions of contemporary thought. The birth of a new idea has always been attended by the publication of scores of papers, followed by a gradual falling off in numbers, as the enthusiasm wanes. Thus interest has been centered successively in the various "forms" of soil water, in mechanical analyses of soils, in adsorption, in base exchange, and, more recently, in the crystalline structures of the various minerals that constitute the soil. The author has explored all these concepts and the data on which they are based. He contends that the data indicate a uniformity of behavior in chemical reactivity, mechanical analysis, and moisture absorption of all soils.

The author conceives of the soil, when freed of extraneous matter, as an acid, the hydrogen of which constitutes an integral part of the hydrated ferroaluminosilicates. He thinks of this hydrogen as being held in no other way than by primary valences. Since the only criterion of an acid is that it must contain hydrogen which is replaceable by a metal, there is no need for making any distinction between a soluble and an insoluble acid beyond a convenience of terminology.

It is now common practice to refer to such acids as silicic, stearic, and uric, when suspended in water, as "acidoids" and to their insoluble salts as "saloids". An acid soil is termed an acidoid because it behaves like an acid in every way, except that it is insoluble in water. There is absolutely no difference, the author says, in the chemical behavior of the acidic hydrogen of a soil and that of any other well known acid. For example:

It will neutralize alkalies, and such neutralization can be followed potentiometrically in accordance with the law of mass action, leading to a perfect titration curve that is characteristic of the soil acidoid.

It can decompose carbonates with the evolution of carbon dioxide, the decomposition proceeding in exact stoichiometric proportions.

It can decompose sulphides with the evolution of hydrogen sulphide, quantitatively and stoichiometrically.

It can hydrolyze esters and bring about the inversion of sucrose in accordance with the catalytic activity of its hydrogen ions.

When neutralized with alkalies, it gives stable saloids with characteristic physical properties, which are similar for all soils. Thus the sodium saloids of all soils are completely dispersed in water but the calcium saloids are not.

When neutralized with alkalies, it gives a heat of neutralization of the same order as that arising from the combination of hydrogen and hydroxyl ions.

Saloids of soil acidoids can be split into cations and anions by the application of an electric current in accordance with well-known laws of "electrolysis", each saloid having a definite "break potential."

The author concludes that natural soils are merely mixtures of saloids of the soil acidoid. Each saloid represents a single point on a titration curve that determines the stage at which it will be neutralized. Being saloids of a weak acid and of comparatively strong bases, they are easily hydrolyzed when they come into contact with water. The extent of this hydrolysis depends on the degree of neutralization. They tend to come to a state of equilibrium that is governed by the amount of rainfall and leaching to which they are subjected. The higher the rainfall the less the degree of neutralization.

Starting with these concepts, the author endeavors to effect a unification of a wide variety of scattered data. The chemistry of soils is reduced to the chemistry of acids and bases and the soil-water system to a solution of soil acidoids and saloids. The soil solution is subject to the laws of acid-base equilibrium. The author visualizes results of the highest practical importance from this approach to the problems of agriculture.

In dealing with the mechanical analysis of soils, some interesting generalizations are developed. Thus, normal sodium saloids of all soils can be dispersed in water to the point of having only primary particles. The formation of these saloids is complete at a pH value between 10.8 and 11.0. No matter what the soil or the preliminary treatment employed on it in preparation for mechanical analysis, one can proceed with certainty that he is dealing with primary particles only, when the pH value of that soil has been raised to the level indicated.

Being certain that he is dealing with the primary particles, one can then proceed with calculations of specific surface. Since the soil acidoid constitutes the surface of ferroaluminosilicates, the total acidic hydrogen on the surface of a unit weight of soil can be calculated. These calculations show reasonably good agreement

with those actually determined by chemical means. This has led the author to define the colloidal state as follows:

"When the mass of molecules constituting the surface of a dispersoid is appreciable as compared to its total mass, that substance is in its colloidal state, and the mass of surface molecules may be designated as its active mass."

This active mass, for all practical purposes, may be regarded as equivalent to a true molecular solution that is capable of taking part in all chemical reactions which are characteristic of its molecules.

In dealing with soil moisture, the author developed the hypothesis that all of it is held by surface tension forces and that it strictly obeys the laws of capillarity. In other words, all soil moisture is capillary moisture, whether it is sucked up from a free surface or absorbed from a humid atmosphere in the vapor phase. Any differences that may be observed are due merely to differences in the sizes of the capillaries in which the water is held. These differences are capable of mathematical interpretation in accordance with the well-known laws of capillarity, which relate the radius of curvature of the liquid meniscus and the negative pressure to which it is subject. This negative pressure may take the form of lowering the vapor pressure or it may be interpreted as free energy. These theoretical deductions lead to the conclusion that all soil water follows the well-known Kelvin equation.

From the geometry of spheres, one can calculate the relation between the diameter of particles and that of the spaces between them. If the size distribution of particles in a given soil are known, one can determine the size distribution of the capillaries within it. Knowing the relation between the size of capillaries and the vapor pressure of the water held in them, as well as the capillary pull, one can work out the complete relation between the moisture absorption at different vapor pressures, the rise of water from a free water surface, and the moisture distribution under free drainage. Having theoretically deduced this, the author then experimentally verified it from the mechanical analysis of soils, irrespective of their origin or type.

Knowing the size distribution of the particles in a soil, one can proceed to calculate its chemical reactivity. Thus the author finds it possible to reach the same conclusion from three independent routes: by the titration curve, the summation values arising from mechanical analysis, and the vapor pressure curve.

This is a brief outline of a comprehensive theory presented in this book. There may not be anything new in it. Other soil workers have held such concepts and still others appear to be veering in that direction. The important point is that the author attempts to present, in lucid form, a theory that takes into account all the physicochemical aspects of the soil system. He has set down a working hypothesis on which future studies can be built.

The author is a very stimulating personality, an interesting conversationalist, and a dynamic speaker. He has the capacity to re-

solve very complicated processes into very elementary concepts. One great advantage of this method of procedure is that it is far less confusing to the beginning student. Thus the man who has been well trained in the fundamental sciences is able to grasp the essentials of this application of science much more readily than would otherwise be possible.

But the book speaks for itself and the author. His data and the conclusions he has drawn from them are presented for inspection. One may agree or disagree with his interpretations and with the principles developed therefrom. Of this one can be sure: a great many of the younger students of soil phenomena will find this a highly stimulating and very thought-provoking presentation on a subject that is of great interest and importance not only to soil physicists and physical chemists, but to research specialists in many other fields as well.

New Brunswick, N.J.
July 18, 1949

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PREFACE

Study of the soil as a distinct branch of natural science is comparatively recent. Less than a quarter of a century ago we were struggling with terminology in an attempt to describe the various phenomena associated with soils. The vast strides made by colloid chemistry at that time gave a fresh impetus to the study of soils, and "adsorption" became a handy term for explaining everything related to soils. The failure of structures erected on clay foundations and the need for cheaper and better dirt roads were two factors that brought the engineer into natural alignment with the agriculturist; and though each still spoke his own language, the common ties began to strengthen.

There are still sceptics who merely laugh and shake their heads at the mere mention of "soil science", and who would prefer to describe it as the application of scientific methods to the study of soil. Science aims at generalization, and judged by that standard the science of the soil is still in its infancy. The present book is an attempt to show that soil science has reached such a stage that, if we are prepared to shake off our prejudices, it is capable of yielding generalizations of far-reaching importance.

In the treatment of the subject I have drawn mostly upon my own work, not because others have not made equally important contributions, but to avoid controversial topics, the book having been written primarily for students of agriculture. Advanced scholars may find it elementary and may hold different views about certain statements made authoritatively. It must be understood that the material has been written for beginners, and is not intended to be a treatise. Facts have been stated and theories have been left in the background, for theories confuse the novice and tax even the initiated.

Unlike other branches of science, hitherto the study of soils has been along rather haphazard lines. At best the accumulation of data has only contributed to the bewilderment of the student whose mental equipment in basic sciences is not prepared to overcome the apparent lack of coherence in the general principles of soil science which he is called upon to grasp.

A student who is made to swallow half a dozen methods of finding the lime requirement or base-exchange capacity of soils is not likely to understand the meaning of soil acidity. It is no fault of his if in the course of time he becomes a blind follower of the whims of the

teachers and is wedded to a particular method for the rest of his life.

I have felt that the training of the youthful mind should be on definite lines against the background of the known laws of the exact sciences with which he is familiar. Once he has grasped the fundamentals, he will be on surer ground for making progress. He must become familiar with generalizations first, and not be confused with exceptions. This textbook has been written with that objective. Whatever its other merits, the science of the soil has not so far yielded results of far-reaching consequence. With all our methods we have still to depend on our "horse sense" or "experience", as we like to call it, for the interpretation of results; and one man's "experience" may be quite at variance with that of another. That we still go on collecting data assiduously is a reflection of our tenacity of purpose rather than proof of progress. We must all look forward to the day when the laboratory examination of a soil will not require the experience of a lifetime for its interpretation. That will happen only when we give students of soil science training in exact methods rather than in "experience".

A. N. Puri

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PART I

CHEMISTRY OF THE SOIL

CHAPTER I

THE SOIL FRAMEWORK

Silicon and aluminum are the most abundant of the elements constituting the earth. If we fuse silica and alumina with some base in a laboratory crucible, we obtain aluminum silicate. Geologists tell us that the earth was once a molten mass of all the elements in their multifarious combinations, which gradually cooled to form a hard crust of varying thickness. No wonder that crust consisted mainly of aluminum silicate! The hard, solid rock of aluminum silicate produced in nature's crucible gradually disintegrated into smaller and smaller particles. The disintegrating forces were of varied origin; the impact of the wind and waves, the expansion and contraction due to temperature changes; the solvent action of gases and vapors in the atmosphere – all contributed their mite in pulling the rock to pieces. This process of breaking down rock by natural forces is called weathering, and it has taken millions of years to reduce the parent rocks to powder consisting of particles of various sizes. This is our soil; chemically it is ferroaluminosilicate of varying composition, with some other elements like sodium, potassium, calcium, magnesium, etc., thrown in. Physically it consists of particles of diameters ranging from 1 mm to 0.00001 mm, in varying proportions.

Soils contain some salts that can be washed out by leaching with water; they may contain moisture which can be readily evaporated away by exposure to heat. They may also contain organic matter which can be burned away, dissolved in alkali, or oxidized by hydrogen peroxide or permanganate. There may be present calcium carbonate, which can be dissolved out by dilute acid. When all the extraneous substances have been completely removed, the residue is what we may call the soil framework. This framework gives mechanical support to the roots of trees and plants. Without this framework vegetation would not stand up, even if it could be supplied with all the nutrient materials.

Let us suppose a soil freed from all extraneous matter by continuous leaching with a dilute acid, everything except the soil framework being removed in a short time. When soils from different localities are subjected to this treatment we find that the soil frame-

work in every case behaves in a similar manner. No matter from what part of the world the soil has been obtained, the properties of its mineral framework differ only in quantity and not in kind. It is not soluble, but its suspension in water behaves like a weak acid in every way and in every case; it is almost equal in strength to acetic acid, though much stronger than boric acid.

What is an acid? According to the classical definition, any compound having one or more hydrogen atoms replaceable by a metal is an acid. The general formula of all acids is HA, in which A is any electronegative atom or group of atoms; thus hydrochloric, sulphuric, boric, stearic, uric, etc., are all acids. Some are more soluble in water than others. Some, like stearic acid, are completely insoluble in water. But whether soluble or not, the one common property possessed by all the acids is that they contain hydrogen atoms which can be replaced by a metal. Since all soils, irrespective of their origin or source, possess this common property the chemistry of the soil reduces itself to the study of its acidic properties, like neutralization with various alkalies and formation of salts; decomposition of carbonates and sulphides; hydrolysis of ethyl acetate and inversion of sucrose; formation of salts with different bases and the properties of the salts thus formed.

For convenience of reference we may call the soil acid "acidoid" and its salts "saloids". It must be remembered, however, that this descriptive terminology is adopted purely for purposes of labeling; it does not imply any fundamental difference from ordinary acids whatsoever: an acidoid exhibits all the reactions characteristic of ordinary soluble acids. The distinction merely lies in the fact that an acidoid is insoluble in water in the ordinary sense of the word. Thus stearic acid is an acidoid, though by definition it is as truly an acid as any other. Similar remarks apply to the distinction between salts and saloids, which must be regarded as exactly alike except that one gives a solution in water and the other only a suspension. As will be explained later, the distinction between a solution and a suspension is also purely arbitrary and disappears at a certain stage; but it is better at this point not to disturb the mental habit of calling a solution a solution and a suspension a suspension.

Like all other weak acids, the salts of soil acidoid are easily hydrolyzed. In nature this happens every day in regions of high rainfall. The carbon dioxide in the water hastens the hydrolysis, and the bases are completely removed in the course of time. In regions of moderate rainfall they are only partially hydrolyzed, and we are left with a mixture of soil acidoid and soil saloid. In the tropics where there is no rainfall, we may find soils which are completely neutralized with bases. All over the world the state of neutralization of the soil acidoid is a function of the rainfall; thus acid soils are characteristic of humid regions and alkaline soils are found in dry tropical countries.

All acids and acidoids give hydrogen ions when dissolved or suspended in water. The concentration of these hydrogen ions deter-

mines the strength of the acidoid and bears a constant ratio to the total un-ionized hydrogen in accordance with the law of mass action in both cases.

In studying the physicochemical properties of acids, our chief interest lies in the behavior of the hydrogen ions, i.e., the electropositive part only. The nature of the electronegative part can be completely disregarded. Similarly in the case of soils we can leave out of account the chemical composition of the complex aluminum silicate. We can perform the elemental analysis, but that leads us nowhere. It might interest the geologist who may be looking for the genesis of the parent rock, but it is of no interest to the plant and it is of no interest to us, at least for the time being. We shall therefore study in the first instance the physicochemical properties of the soil acidoid and its various saloids.

CHAPTER II

SOIL ACIDOID

pH Value and Titration Curves

We have already seen that all acids and acidoids contain hydrogen as one of the constituents; and the properties which characterize them are due to the presence of hydrogen ions. When an acid or acidoid is dissolved or suspended in water, a certain proportion of it splits up into electropositive and electronegative ions, the former being always hydrogen. It is evident that in a given solution the total number of hydrogen atoms determines the quantity of acid or acidoid present, whereas the number of hydrogen ions determines its strength or intensity. In other words the greater the percentage of the acid or acidoid splitting up into ions, the greater its strength, and vice versa. Strong acids, therefore, are those which split up into ions to a larger extent and contain a higher concentration of hydrogen ions.

The hydrogen ion concentration of a solution may vary from one gram per liter to as low as 0.00000000000001 gram per liter, and the methods of measurement are so surprisingly accurate that variations within this range can be measured. The total range of variations, however, is so large that the figures become unmanageable. We therefore make use of the pH scale. The following table shows the relation between pH and hydrogen ion concentration.

Hydrogen ion concentration (gram per liter)		pH
1	10^{0}	0
0.1	10^{-1}	1
0.01	10^{-2}	2
0.001	10^{-3}	3
0.0001	10^{-4}	4
0.00001	10^{-5}	5
0.000001	10^{-6}	6
0.0000001	10^{-7}	7
0.00000001	10^{-8}	8
0.000000001	10^{-9}	9
0.0000000001	10^{-10}	10
0.00000000001	10^{-11}	11

0.000000000001	10^{-12}	12
0.0000000000001	10^{-13}	13
0.00000000000001	10^{-14}	14

The pH value, therefore, is the number of digits after the decimal point, or the negative index of 10 if expressed mathematically. It will be seen that, though 1 is ten times 0.1, a hundred times 0.01, and a thousand times 0.001, and the change involves 1000 divisions on any scale or yardstick, by having recourse to the pH scale, the change involved in going from a hydrogen ion concentration of 1 to that of 0.001 gram per liter is reduced to three divisions of the scale, and the total change in the pH range is reduced to 14 divisions only. This is a great convenience in plotting.

There is another curious fact about the hydrogen ion concentration: there is always an equilibrium between hydrogen ion concentration (H) and hydroxyl ion concentration (OH) in water solution, so that the product (H) times (OH) is always constant. Thus if the concentration of one increases, that of the other must decrease correspondingly to maintain a constant value of the product of the two. It is the preponderance of one or the other that determines the acidity or alkalinity of a solution or suspension. Actually pure water is neither acid nor alkaline; in other words the concentration of hydrogen and hydroxyl ions in pure water is just about equal, each being 10^{-7} gram per liter, or pH 7. Therefore, by common consent pH 7 is considered to be the neutral point, and any solution having this value is neither acidic nor alkaline. Above pH 7 the alkalinity increases, and below it acidity increases; therefore a solution having a pH value of 5 is more acid than one having pH 6, and so on.

When a strong acid is added to a strong base in equivalent amount the resulting salt is neutral, i.e., it is neither acidic nor alkaline, and its pH value is close to 7. However, if a weak alkali is added to a strong acid in equivalent amount, the resulting pH value is not 7, and may be considerably less. In other words the chemically equivalent point is not identical with the neutral point on the pH scale. Thus a strong acid like hydrochloric may be chemically neutralized at a pH value in the neighborhood of 4; on the other hand the equivalent point of a weak acid like boric might lie in the vicinity of pH 11. It is clear, therefore, that for a given strong alkali, the weaker the acid, the higher the pH value of the resulting solution when an equivalent amount of the alkali is added to it.

It is a problem to find the equivalent point of an acid or acidoid. If the pH value of the neutral point is known we can add an indicator, which changes color at that point, and by gradually adding the alkali in the presence of the indicator the equivalent point can be located. This is possible because at the equivalent point an abrupt change in pH value may occur, but this is not always the case. If the solution or suspension is colored, the equivalent point can be located by adding increasing amounts of alkali to a known amount of the acid

and measuring the pH value at every addition. Thus is built up what is known as the titration curve and the point of inflection on the titration curve determines the equivalent point. The pH value at every step can be determined electrometically with the hydrogen or the glass electrode.

In the case of weak acids, the point of inflection at the equivalent point is not sharp, and it becomes difficult to decide what is the exact point of neutrality. The end point of titration of such acids can be found by making use of a method developed by Harris and discussed by Britton in his monograph on hydrogen ions. The main conclusion on which the method is based is that for weak acids neutralization with a strong base takes place between two definite pH values; that is, for monobasic acids the pH interval between the beginning and the end of a titration is 4. It is therefore necessary to titrate only between these limits to obtain the neutral point.

Titration curves furnish very important sets of values for expressing the characteristics of soil acidoids. The equilibrium between soil acidoid and alkali added to it is not established quickly; therefore the results obtained by the incremental additions of alkali and pH determination after each addition cannot be relied upon. Increasing amounts of alkali must be added to weighed portions of the soil and the pH determined when the equilibrium is established.

Natural soils are already partly neutralized with bases; therefore they are not suitable as such for determining the titration curve of the acidoid. The saloids must first be converted into acidoid to obtain the complete titration curve. This is easily accomplished by leaching the soil with 0.05N HCl until the leachate is free from calcium ions, and then leaching with water until the leachate is free from Cl ions. A final washing with a little alcohol insures easy drying of the sample, which is readily detached from the filter paper. Ten grams of the soil is sufficient for determining the entire titration curve. One-gram portions of the dried soil acidoid are taken with 10 cc of sodium hydroxide solutions of increasing concentration. The mixture is shaken for 48 hours continuously in a mechanical shaker or intermittently with the hand. After this the pH values are taken with the glass electrode. The actual determination of pH value with the glass electrode does not take long, and more than a dozen soils can be examined in a day. It is a good plan to make a rough determination of the approximate equivalent point by adding standard NaOH gradually to 1 gram of soil suspended in water, using phenolphthalein as indicator. This indicator is quite suitable unless the soil is very dark in color. Even in that case a drop of the indicator on the surface of the suspension at once shows the color change if the neutral point has been reached. This is only a rough method to give an idea of the approximate amount of total alkali to be used in the final concentration, and how the incremental quantities should be spaced to obtain more values near the point of inflection.

Typical titration curves of a black cotton soil (P.C.13) are shown in Figures 2 and 3 and speed of reaction between soil acidoid and NaOH in Figures 1 and 4.

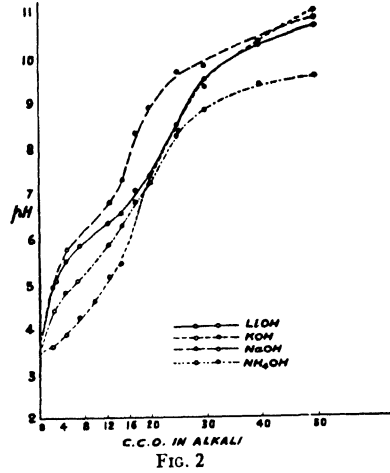
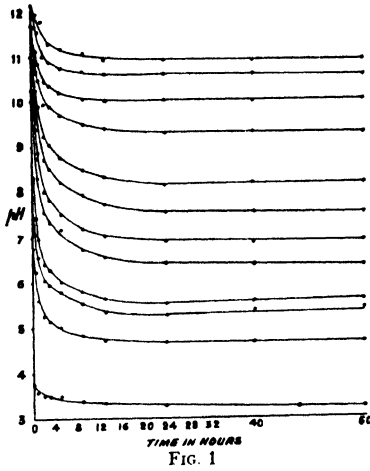



Fig. 1. Speed of Reaction between Soil P.C. 13 A.T. and Sodium Hydroxide
Fig. 2. Titration of Soil P.C. 13 A.T. with Hydroxides of Monovalent Ions

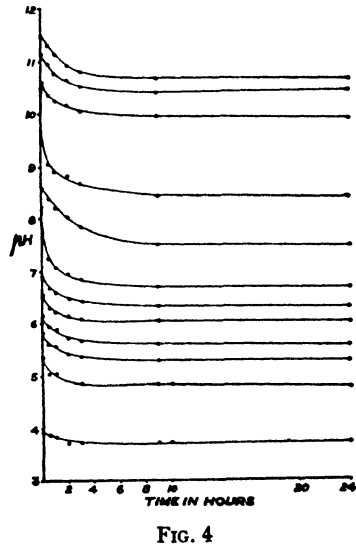
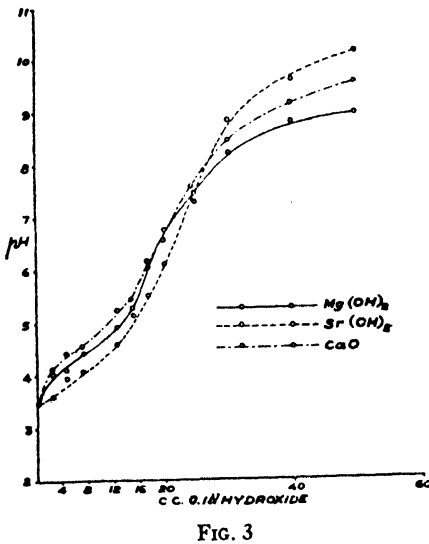



Fig. 3. Titration of Soil P.C. 13 A.T. with Hydroxides of Divalent Ions
Fig. 4. Speed of Reaction between Clay Acidoid and Sodium Hydroxide

It will be seen that the characteristic shape of the curve is maintained with every base, although different proportions of alkali are required to produce a particular pH value with various ions. This is in agreement with the observations made on weak acids like boric. The actual trend of the titration curve depends on the nature of the alkali used, although the end point must be reached with the same amount of alkali in every case. From Figures 2 and 3 it is apparent that the neutralization point occurs at pH 7.5. It is also seen that although the inflection in the curve occurs at this point, the titration is by no means complete. This is a clear indication that in the case of soil we are dealing with dibasic acidoids. It must be emphasized that the inflection in the curves is even more marked than that in the titration curves of several dibasic acids, such as succinic and tartaric, and is at least as marked as that in the titration curve of malonic acid.

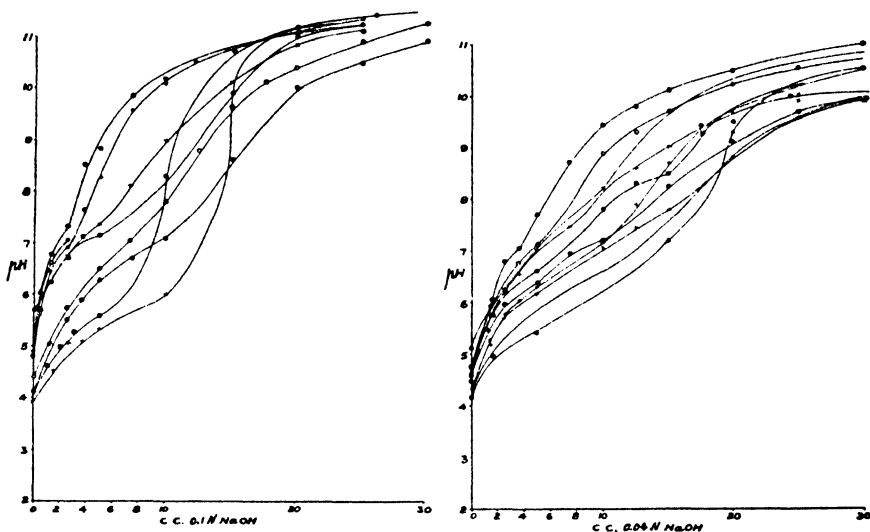
Nothing in these curves shows that the acidoids behave any differently from other weak acids. The slowness with which equilibrium is reached is to be expected from the fact that the cohesive forces between the individual particles forming aggregates resist the entry of the alkaline solution, which can take place only after prolonged shaking. There is no doubt that equilibrium is established if we wait long enough. That the speed of reaction is dependent on the state of aggregation is shown by the fact that a dispersed clay suspension takes about 9 hours to come to equilibrium as against 48 hours required by the undispersed soil.

Titration curves of several soils were determined after the usua acid treatment, followed by leaching with water. Some typical re sults are shown in Figures 5 and 6. Each of these curves showed an inflection at a point approximately 4 pH units higher than that of the original acidoid. The acidoid equivalent of these soils (T/2) may be determined by interpolation at $(a+4)$, when a is the pH value of the soil acidoid without the addition of any alkali.

A closer study of the titration curves of soils will indicate that what is known as the "base-exchange capacity" of soils has no theoretical significance even if it refers to an arbitrarily fixed uniform pH value. The neutralization point of different acids lies at different pH values; this is true also for soils. The acidoid equivalent must constitute one of the fundamental constants for characterizing soils. It could be determined by merely converting the soil saloids into the acidoid and then titrating potentiometrically with NaOH to a pH value 4 units higher than that of the acidoid. Since it is a dibasic acid, this alkali titre must be multiplied by 2 to obtain the acidoid equivalent. Complete neutralization of the acidoid takes place at such a high pH value that for all practical purposes only neutralization of the first hydrogen need be considered.

"Exchangeable bases", "exchangeable hydrogen", "base-exchange capacity", "degree of saturation" and "saturation capacity" unfortu-

nately are terms so extensively used in soil literature that any attempt to discard them completely may prove abortive. We can, however, impart to this terminology a more fundamental background by giving it a new orientation in the light of the titration curves of the soil acidoids. Accordingly the various terms may be interpreted as follows.

Total exchangeable bases in a soil are equivalent to that portion of the acidoid already neutralized with bases; in other words the saloid equivalent. "Base-exchange capacity" is equivalent to the total base required for the formation of the mono-acid saloid (T/2) value). "Degree of saturation" represents an acidoid saloid ratio corresponding to the point on its titration curve which is represented by the pH value of the natural soil. "Saturation capacity" is

Figs. 5 and 6. Titration Curves of Various Soil Acidoids

equivalent to the total base required for the formation of the normal saloid (T). "Exchangeable hydrogen" is the alkali equivalent required to neutralize the soil to a pH value corresponding to that of its T/2 value.

These interpretations are fundamental and bear no reference to any particular method of estimation. A clarification of the issue, it is hoped, will lead to a greater refinement of the technique in the determination of characteristic constants for soils. This will result in a better agreement between the various methods, for it must be admitted that if two or more methods for the measurement of a certain constant give consistently different results, the error is not in the methods, but in our conception of the constant we are measuring. Any progress in the methods of measurement, there-

fore, can result only from a clear knowledge of what we want to measure. The main difficulty in making soil measurements has been that we measure something first and then give it a name; the measurement changes, but the name remains. We can even draw the titration curve of a soil acidoid backward. For this purpose, the forward curve may be obtained by neutralizing the acidoid with $Ba(OH)_2$ and then back-titrating with H_2SO_4. Such a curve is given in Figure 7.

It will be seen that the back-titration curve is lower than the forward curve, but that in other respects it is similar. The fall in pH value at every stage is due to the slight solubility of $BaSO_4$, which lowers the pH value by suppressing the ionization of the saloid. This explanation is supported by the fact that the titration curve of a clay suspension with NaOH showed a similar shift when some $BaSO_4$ (Pro Röntgen) was added to it. This curve is shown in Figure 8.

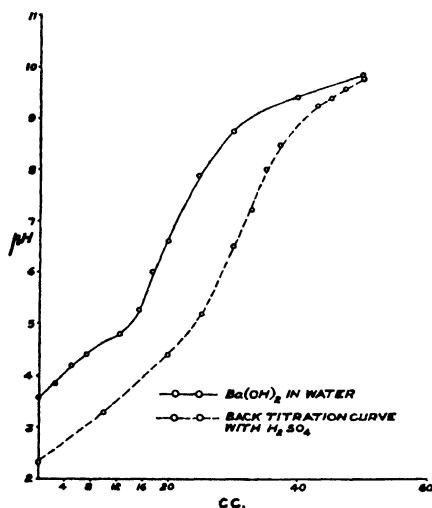



Fig. 7. Titration Curve of Soil P.C. 13 A.T. with Barium Hydroxide

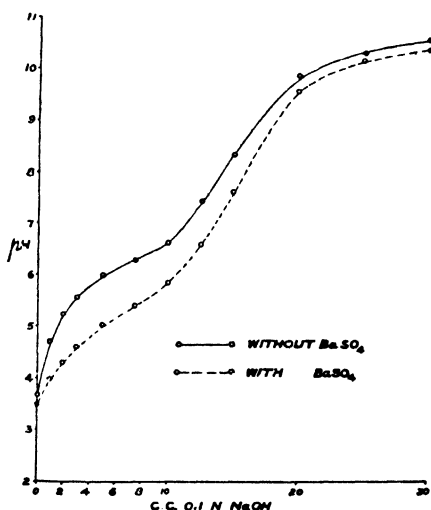



Fig. 8. Titration Curve of Clay Acidoid with Sodium Hydroxide with and Without Barium Sulfate

It is remarkable that even the slight solubility of $BaSO_4$ should cause such an appreciable shift in the pH value. The results might seem to throw some doubt on the colorimetric method of Kuhn for determining pH values in the presence of excess $BaSO_4$. In actual practice, however, probably no such shift in the pH occurs, because ordinary soils already contain sufficient quantities of salts to have caused the initial lowering of the pH value, and the added amount of $BaSO_4$ would not have much effect. It is only in the absence of salts that even the slightest additions would produce change.

Dissociation Constants of Soil Acidoids

The titration curves of weak acids having dissociation constants of less than 10^{-4} with strong alkalies like NaOH are defined by the usual mass law equation:

$$pH = pK \log salt/acid$$

Hence when the acid is half neutralized, i.e., the ratio salt/acid is unity, pH = pK. Thus the pH value of a weak acid when it is half neutralized with NaOH is equal to the logarithm of the reciprocal of its dissociation constant. Just as pH is used for comparing the intensity of acidity of different solutions, pK values could be used for comparing the activity of the acids or acidoids, so that the higher the value of pK the weaker the acid. It might be noted that although the pH values of soils change with the state of neutralization of the acidoid, the pK values are fundamental constants that could be used for characterizing soils. Such values determined from their titration curves for a number of soils are given in Table 1. The pK

Table 1. Acidoid Equivalent (/2) of Soils and Their pK Values.

Soil No. P.C.	Clay (%)	per 100 gm. soil (/2) (m.e.)	per 100 gm. clay (/2) (m.e.)	pK
1	11.3	12.00	106.2	6.81
2	59.3	54.40	91.7	4.90
3	62.2	61.00	98.1	5.00
5	19.3	10.56	54.7	6.70
6	28.4	11.80	41.5	7.18
7	21.8	7.30	33.4	7.82
8	25.2	19.60	77.8	5.78
9	21.6	7.70	35.5	7.30
10	35.6	19.80	55.6	5.63
11	32.8	26.00	79.3	5.49
12	7.2	4.90	67.8	7.25
13	58.9	40.00	67.9	6.40
14	21.5	24.00	116.3	6.75
15	22.4	5.70	25.4	7.55
25	4.0	3.76	94.0	9.75
Acetic Acid				4.7
Uric Acid				5.8
Hypochlorous Acid				7.4
Boric Acid				9.2
Phenol				10.0

values of some common acids are also given for comparison. It will be seen that some soil acidoids are as strong as acetic acid, the majority are only slightly weaker than uric acid, and only very few are as weak as boric acid.

If the dibasicity of soil acidoids is assumed, then these values should be denoted as pK_1, referring to the dissociation constant of the first hydrogen atom. The dissociation of the second hydrogen

atom is so feeble that the normal saloids would be strongly hydrolyzed. The pK_{11} values, therefore, can be of only theoretical interest, but they can be determined by adding another half equivalent of NaOH to the acidoid already neutralized to the stage equivalent to T/2 (i.e., the first hydrogen atom) and measuring the pH value. However, for the time being we can consider that the pK values of soils refer to the dissociation of the first hydrogen atom. It is to be remembered that in soils we may have mixtures of acidoids of slightly differing pK values; but in the absence of specific information on this point it is convenient to consider that we are dealing with one acidoid having a definite pK value determined by the titration curve.

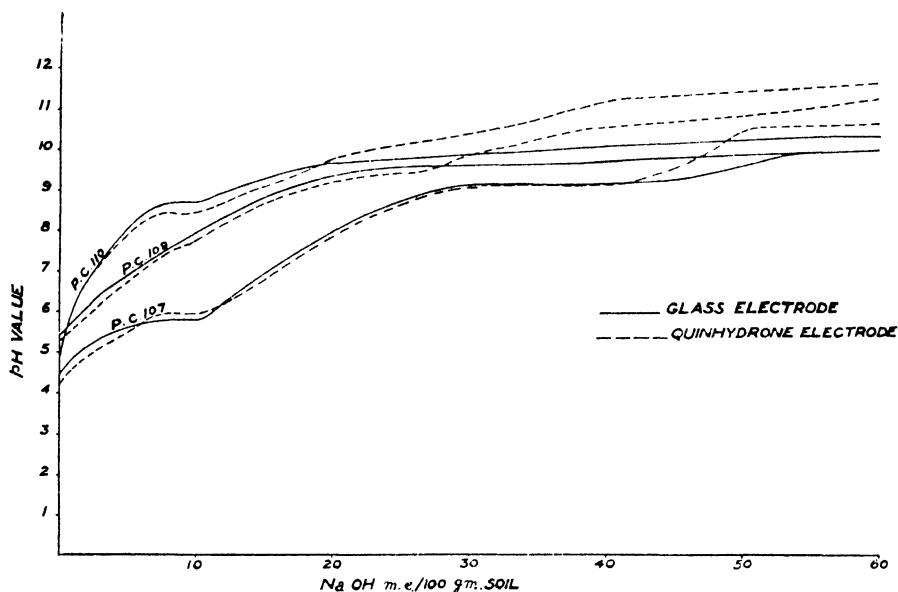



Fig. 9. Titration Curves of Soils with the Quinhydrone and the Glass Electrode

Titration curves have not been introduced extensively in the routine analysis of soils so far. These measurements should receive greater attention from soil scientists as a basis of soil classification. The titration curve of a soil acidoid is not only reproducible but easily determined by the following technique. Twenty to 30 grams of soil are treated with enough acid to break up all the carbonates. The treated soil is transferred to a Buchner funnel and leached with 0.05N HCl in 100-cc lots until the filtrate is free from calcium ions. It is then leached with water until free from Cl ions, and finally with a few cc of alcohol to facilitate drying and to prevent caking. The leaching is preferably done without suction, and the filter paper is attached to the funnel by running a little

molten wax around the edges. The soil on drying is easily detached from the filter paper, and 2-gram portions of the treated soil are shaken for 48 hours with 10 cc of NaOH solution containing increasing amounts of alkali. The pH values are determined with the quinhydrone or glass electrode. From the titration curve thus obtained, the T/2 value (acidoid equivalent) is interpolated at a point 4 pH units higher than the initial pH. It is rather surprising that the quinhydrone electrode can be used for pH values up to 9, and as will be seen from Figure 9.

The titration curves are almost identical with those obtained by the glass electrode. Although the newer types of glass electrodes are extremely simple to use, some laboratories may prefer the use of the quinhydrone electrode, which is entirely satisfactory up to the pH range required for the titration curves of soils.

In the titration of a weak acid or acidoid with a strong base some hydrolysis takes place. This causes the titration curve in the vicinity of the end point to fall slightly above the "salt line" and thus tends to render the position of the end point somewhat uncertain. The extent of this hydrolytic action depends on the temperature, concentration and dissociation constant of the weak acid.

CHAPTER III

INTERACTION BETWEEN AMMONIA AND SOIL ACIDOIDS

Titration with Ammonia

In titrating a weak acid with a weak base, though the salt formed may be appreciably hydrolyzed, the products of hydrolysis are too weak to furnish the solution with ion concentrations comparable in magnitude with those set free by the unhydrolyzed salt. The titration curves in such cases coincide with the salt lines and do not diverge from them until the end point is nearly reached. These facts indicate that if the titration of soil acidoids were carried out with a weak base, like ammonia or magnesia, a much more distinct "break" might be furnished at the end point, than when strong alkalies are used. Titrations with these bases can be performed both conductometrically and electrometrically. A typical curve is shown in Figure 10.

A word about the conductometric titrations. The Kohlraush bridge is well known. The simple electrometric arrangement by which a direct current of high voltage is used has been described by the author (1937).* In the curve shown in Figure 10 the latter metnod was used, and the conductivity values are in terms of arbitrary salinometer readings. Conductometric titrations with $Mg(OH)_2$ are not possible, as the conductivity of the suspension is too low for accurate measurements.

The effect of soil-water ratio on the equivalent point was tested in two different soils, by both electrometric and conductometric measurements. The results show that the soil-water ratio has practically no effect on the base equivalent of soil acidoids.

It will be seen that the position of the end point can be found by producing the straight portions of the two branches until they intersect. The graphical method is likely to furnish more exact values than the interpolation to 4 pH units employed when titrations are carried out with NaOH.

The equivalent point determined by NaOH titrations is referred to as the T/2 value on the assumption of the dibasicity of soil acidoids. The second hydrogen atom, however, would easily hydrolyze and would not exist in natural soils subject to leaching. A weak base like ammonia would hardly combine with an extremely

*Soil Sci., 44:241 (1937).

weak acid, represented by the second hydrogen in soil acidoids, and would directly furnish values comparable with the T/2 values determined by titration with a strong alkali.

Since, as we have seen, the base equivalent of soil acidoid marks the limit of hydrolysis, any alkali added over and above that value would be easily leached out with water. This fact indicates the possibility of trying other methods, which though different from those outlined above, are likely to give the same result. Of these the most fruitful would appear to be those in which an excess of alkali is added to the acidoid, the excess being removed subsequently, leaving behind only that amount which has combined up to the limit of hydrolysis. In the list of bases that might be tried for the purpose ammonia occupies a unique position; as it is volatile,

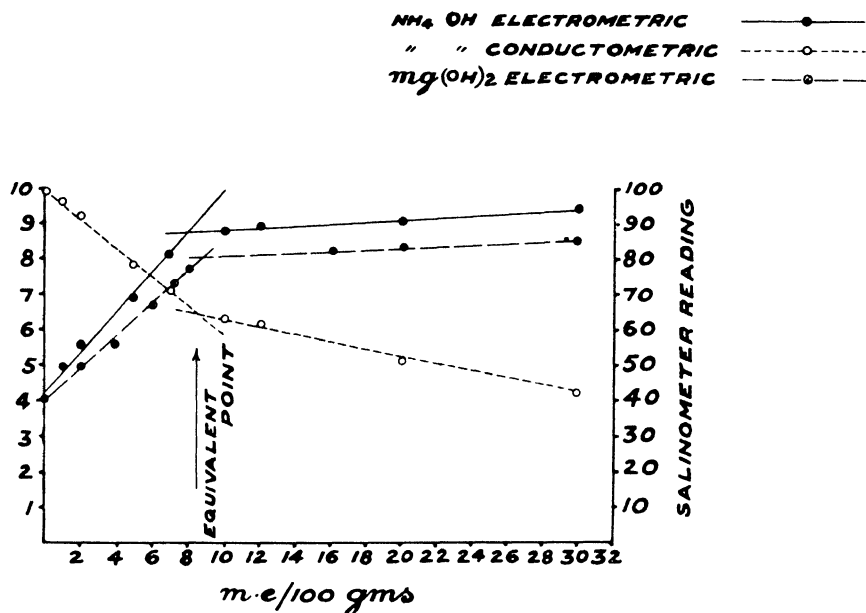



Fig. 10.

both removal of the excess by heating or aeration and estimation by displacement with a stronger alkali are easy matters. As pointed out before, ammonia is a weak alkali; with weak acids it must show considerable hydrolysis. We can, however, determine the extent of the reaction up to the limit of hydrolysis by adding excess ammonia and removing the hydrolyzed and unreacted part by aeration or boiling. Results with a number of common acids, soluble as well as insoluble, may be cited by way of illustration.

A known weight of the dry acid is placed in a desiccator over ammonia solution for 48 hours. After this it is placed over H_2SO_4 in a desiccator; the excess ammonia is taken up by the H_2SO_4 and

the amount left with acid under test is supposed to have reacted up to the limit of hydrolysis. The ammonium salt of the acid is then distilled with lime and the ammonia driven out is taken up in standard acid which is then back-titrated. Results with typical acids are given in Table 2 in terms of the percentage of the equivalent amount of acid reacted with ammonia.

It will be seen from Table 2 that strong acids are completely neutralized below pH 7. For weaker acids the amount of ammonia used is about 50% of the theoretical amount required for neutralization (except boric acid, for which the value is 33%). In such cases the pH value of the ammonium salt formed is about 8, or a little over. It is significant that in no case is the amount of ammonia taken up more than the equivalent amount required for neutralization.

Table 2. Interaction between ammonia and various acids

Acid	% acid reacted with ammonia	pH of ammonium salt
Boric acid	33.5	8.84
Uric acid	45.0	7.80
Phenylacetic acid	99.2	5.66
Stearic acid	49.5	8.66
Salicylic acid	50.0	8.24
Sulphanilic acid	99.6	9.24
Picolinic acid	99.8	8.04
Thiosalicylic acid	49.2	5.60
α-Picolinic acid	98.7	7.32
Picramic acid	93.6	5.98
Sebacinicum acid	80.0	5.82
Citric acid	98.6	6.34
Thiobenzoic acid	97.7	7.56
Phthalic acid	99.8	8.04
Oxalic acid	100	6.00

In order to establish the relation between ammonia reaction and the pH value of an ordinary buffer solution, the universal buffer mixture of Predeaux and Ward (B.D.H.), brought to different pH values with NaOH, was used. The procedure in every case was to add excess ammonia to the buffer, boil to half the volume, and then, after adding excess lime, to determine by distillation the ammonia retained. Preliminary experiments had shown that when a solution of ammonia is boiled until the volume is reduced to half, all the free ammonia is driven off.

The results with the universal buffer mixture are given in Figure 16 along with the ordinary titration curve of the buffer mixture with ammonia. It will be seen that the ammonia which reacts with the buffer solution is a function of the pH value, and in fact denotes the residual portion of the titration curve when a part of the solution has been neutralized with NaOH. It is seen that no ammonia is taken up by the buffer solution above pH 9.

To return to the soil acidoid, four typical soils were selected for parallel experiments: a black cotton soil (P.C. 13), an alkaline alluvium (P.C. 61), a laterite (P.C. 6), and a clay alluvial sub-soil (P.C. 123). These soils were treated with 0.05N HCl, as usual, to convert them into the acidoids. The titration curves of the acidoids with NaOH and ammonia are given in Figures 11-16.

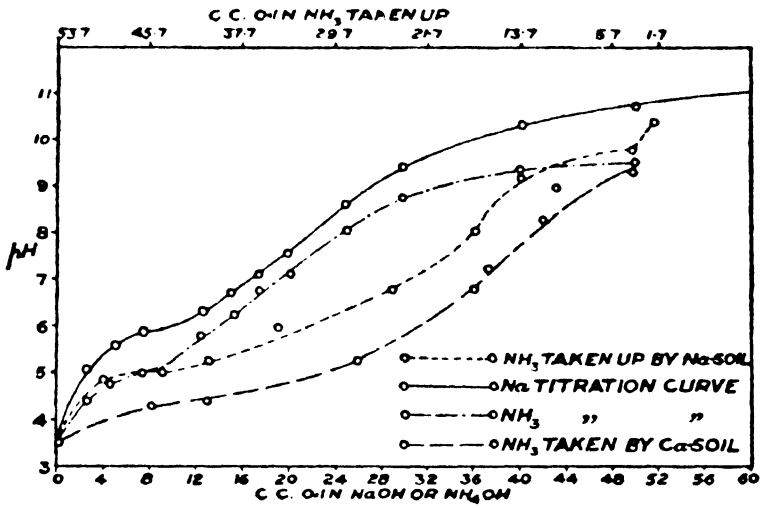



Fig. 11. Titration Curves and Ammonia taken up by Soil P.C. 13

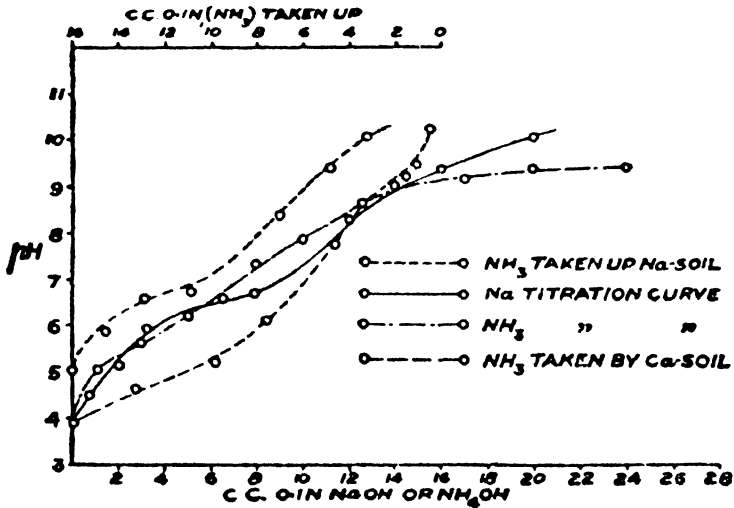



Fig. 12. Titration Curves and Ammonia taken up by Soil P.C. 61

The soil acidoids were also gradually neutralized with different bases, the suspensions shaken for 48 hours, and pH values determined. Then 10 cc of normal ammonia solution was added to each

suspension, and after 48 hours the suspension was boiled to half the volume. Ammonia was then determined in the usual way by distillation with lime. In the case of soil P.C. 13, increasing amounts of

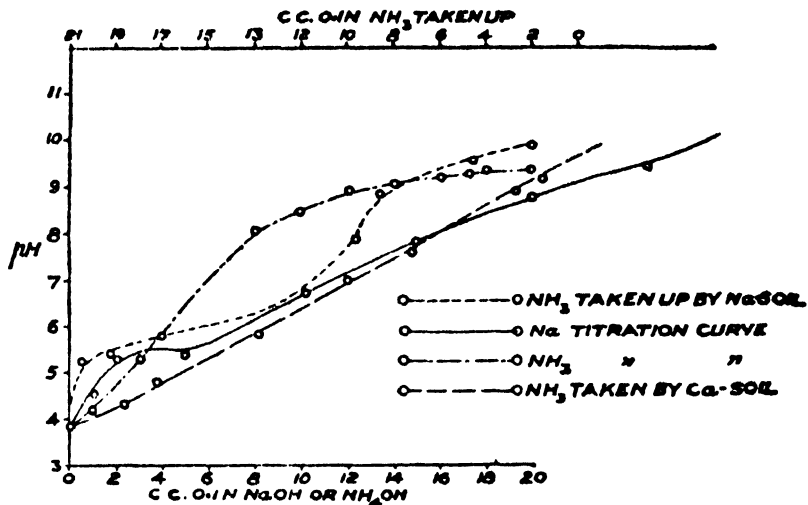



Fig. 13. Titration Curves and Ammonia taken up by Soil P.C. 6

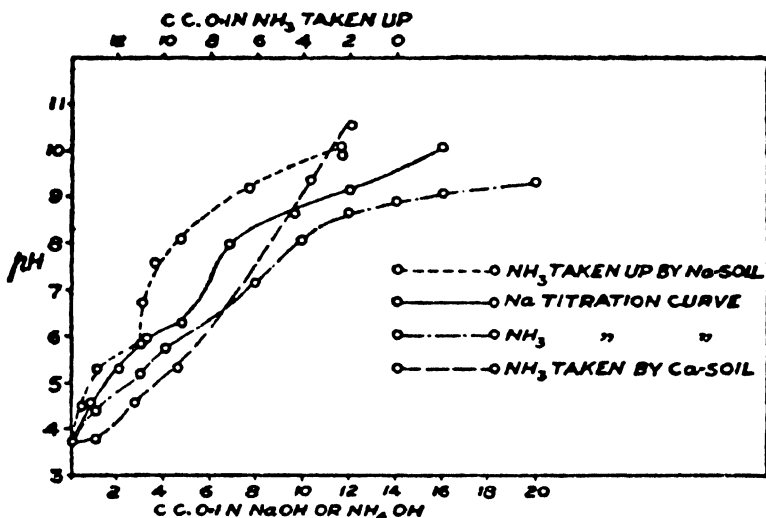



Fig. 14. Titration Curves and Ammonia taken up by Soil P.C. 123

the hydroxides of Na, Ca, Mg, Sr, and Li were used to obtain different pH values; with the other three soils only hydroxides of Na and Ca were used. These results are plotted in Figure 16, along with others and show the characteristic shape of the residual titration curves. Straightforward curves in every case are also given for comparison.

The experiment was repeated for Na and Ca ions by allowing the acidoid to take up ammonia by adding and boiling the excess, and then adding increasing amounts of NaOH and $Ca(OH)_2$, followed by boiling. These results are plotted in Figure 16. (NaII and CaII) show that the final equilibrium is the same whether ammonia is added after the addition of NaOH and $Ca(OH)_2$ or before. It is also evident that a certain amount of $Ca(OH)_2$ or NaOH added to ammonia soil saloid does not drive out an equivalent amount of ammonia. Obviously the relation between the ammonia taken up and the amount of saloid in the soil is valid only when the pH value and not the percentage of alkali added is taken into consideration.

From an examination of several soils, it has been concluded that soil acidoid, when shaken with excess ammonia and boiled to half

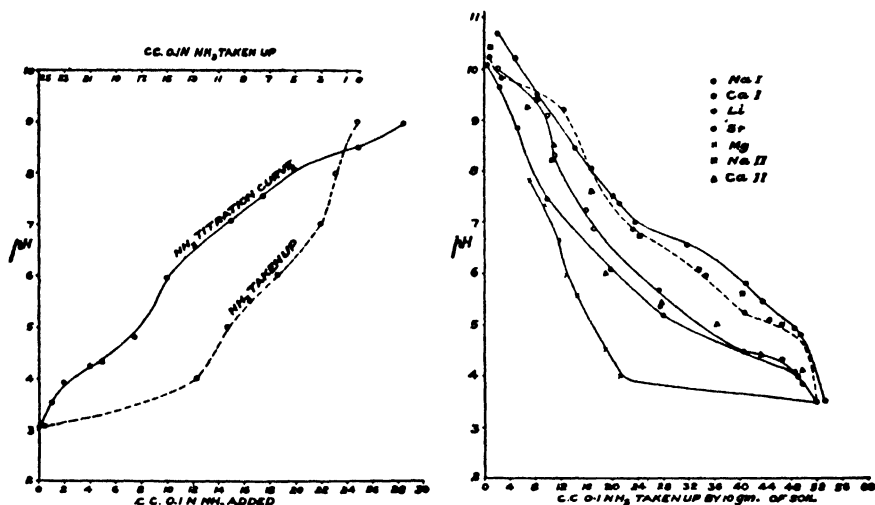



Fig. 15. Titration Curve of B.D.H. Buffer with Ammonia

Fig. 16. Ammonia Taken up by Na-, Li-, Sr-, Ca-, and Mg-Soils (P.C. 13)

the volume, retains an amount equivalent to T/2, as determined by titration curves with NaOH. The final pH value of the ammonia saloid varies between 6 and 8. This variation would be expected if we suppose that the strength (dissociation constant) of the acidoid in different soils is different.

Experiments with ammonia conducted at the boiling temperature are simpler, as at ordinary temperatures the rate of removal of excess ammonia is extremely slow. However, there are certain advantages in carrying out the experiments at room temperature, as the conditions are more natural and the danger of side reactions is minimized. The following method may be used to bring about the reaction with ammonia in the cold. A weighed amount of

the acidoid is kept in a flat dish over normal ammonia in a desiccator for two days. It is then transferred to another desiccator and kept over 90% H_2SO_4 under vacuum for 48 hours. The ammonia retained by the soil is then determined by distillation with lime in the usual way. The results of ammonia reaction with some typical soils after conversion into acidoid are recorded in Table 3, which also gives the clay contents and pH value of the original soil, as well as its ammonium saloid.

Table 3. Interaction between Ammonia and H Soils

Soil P.C.	Clay (.002mm) (%)	Ammonium Saloid m.e. per 100 gms	pH Value	
			Natural Soil	Ammonium Saloid
1	11.3	5.3	8.45	8.21
3	62.2	63.1	7.64	8.01
4	15.2	8.2	8.55	8.40
5	12.2	7.3	8.77	8.44
6	28.4	11.0	5.29	8.14
7	21.8	7.1	9.58	8.88
8	25.2	18.7	8.41	8.36
9	21.6	8.1	5.76	7.74
10	35.6	25.1	8.71	8.28
11	32.8	23.7	8.77	8.55
12	7.2	4.6	5.83	7.83
15	22.4	14.3	7.71	7.97
16	8.7	4.9	8.74	8.44
17	14.1	8.2	8.20	8.32
18	22.6	11.7	5.79	8.19

It is clear that, except in the case of naturally acidoid soils or at the other extreme natural Na saloids, the pH value of the original soil is approximately the same as that of the ammonium saloid. The reason is not hard to find. In almost all cases where the agreement is apparent, the soil contains excess $CaCO_3$ and is in fact a Ca saloid, in the sense that any excess of Ca added to it in the form of hydroxide will either be converted into carbonates or washed down if the soil is subjected to leaching. In other words, it represents a limit beyond which any base present will be easily hydrolyzed and removed by leaching. The mechanism of ammonia reaction is similar; the soil is allowed to take up an excess, and the easily hydrolyzable portion is removed under vacuum over H_2SO_4. Thus the soil comes to equilibrium at a pH value not far from that under natural conditions in the presence of excess $CaCO_3$. However, in the case of soils having no $CaCO_3$ or containing Na saloids, the pH value in the natural state may be too low or too high compared to that obtained with the ammonium saloid.

It must be pointed out, however, that the difference between hydrolyzable and non-hydrolyzable bases is only one of degree, and there is no reason to suppose that almost all the bases will not be removed provided the leaching action is sufficiently prolonged.

Another point worthy of note in this connection is that the removal of bases by simple leaching depends entirely on the mutual reaction of the two bodies, i.e., only if the pH value of water is lower than that of the suspension of soil in water, will bases be removed by leaching with that water.

In nature the latter condition is generally insured by the presence of CO_2 in water. Soils subjected to the leaching action of rain water, therefore, develop acidity. Under conditions of artificial irrigation the quality of irrigation water must determine the reaction of the soil.

It is interesting to note that the pH value of the ammonium saloid for most soils is in the neighborhood of 8.5, but is appreciably lower in the case of all humus and laterite soils. It would thus appear not only that acidity in such soils is produced by their peculiar geographical condition of being situated in humid regions, but that the nature of the acidoids in them is such that if converted into saloids, they would tend to hydrolyze at a lower pH value than others. It is also seen that the pH values of the ammonium saloids, on the whole, are higher when the reaction takes place in the cold than when the excess is removed by boiling.

Base Exchange

The term "base-exchange capacity" is rather loosely applied in soil literature. Very often it is confused with "saturation capacity" and not infrequently is identified with "total exchangeable bases". As pointed out before, "base-exchange capacity" must refer to the power of the soil to combine with bases in such a manner that they cannot be easily removed by simple leaching with water, but can be readily exchanged by an equivalent amount of other bases. In other words, it represents a limit beyond which the saloid would be easily hydrolyzed. It can, therefore, be determined by adding excess of base to the soil, followed by exhaustive leaching with a neutral salt, until the exchangeable ions have been replaced by the basic portion of the neutral salt. The excess of the salt is then washed out with water or alcohol, the soil leached with another neutral salt, and the displaced ions determined in the filtrate. The success of the method and the choice of the neutral salt must depend upon the ease with which a particular ion can be determined analytically.

So far the only salt used for this purpose has been ammonium chloride or acetate. This is because combined ammonia is comparatively simple to estimate. However, the process of washing the excess ammonium salt before the final estimation is not only tedious but is liable to error because of the difficulty of carrying it to completion. The same objective can be gained in a much simpler way. If excess KOH is added to the soil followed by leaching with KCl solution, K saloid of the soil is formed. If this K saloid, without the removal of the excess KCl, is leached with ammonium carbonate, we get the ammonium saloid of the soil, and the displaced

K_2CO_3 appears in the filtrate along with excess ammonium carbonate. The latter is easily removed by boiling and the K_2CO_3 titrated with standard acid, which is equivalent to the T/2 value of the soil. We may call it "base-exchange capacity" to satisfy a mental whim and the habit of usage, but it has no further significance than the base equivalent of the soil acidoid. Since there are several methods of finding base-exchange capacity which do not give the same result, in referring to this constant (if it is a constant) we must specify the method used. There is no doubt that some of these methods do give values agreeing with the base equivalent of the soil acidoid, but it is due to accident rather than design. Those methods might be retained, but the terminology must be discarded.

We have seen that the formation of ammonium saloid marks the neutralization of the soil acidoid up to T/2. It has also been pointed out that the pH value of the soil in contact with excess $CaCO_3$ or the Ca saloid of the soil is of the same order as that of the ammonium saloid of the same soil. Since most agricultural soils are mainly Ca saloids, we could determine the pH value of the natural soil with a certain degree of accuracy by converting it partially into the ammonium saloid by allowing the natural soil to take up excess ammonia, the excess being subsequently removed by placing it over H_2SO_4. We could also change the soil entirely into the ammonium saloid by first converting it into the acidoid.

If S and T are the amounts of ammonia taken up by the natural and the acid-treated soil respectively, then obviously (T - S) will be the amount of base already present in the natural soil, which is that particular point on its titration curve represented by the pH value of the natural soil. If T represents the equivalent of the total ammonium saloid, then we can state the formation of the ammonium saloid in the natural soil as a percentage of the total, (V). Thus $V = \frac{100\ (T - S)}{T}$. The possible correlation of (V) with pH value of the natural soil was studied with 57 soils of various types. For comparison the following methods of finding the pH value of the soils were used:

(1) Hydrogen electrode; 1:5 soil-water ratio; 2 hours' shaking (H).

(2) Quinhydrone electrode; 1:1 soil-water ratio; 2 hours' shaking and standing overnight (Q).

(3) Antimony electrode; 1:1 soil-water ratio; 2 hours' shaking and standing overnight (Sb).

(4) Colorimetric method; 1:5 soil-water ratio; occasional stirring and standing overnight. Clear solution obtained by filtering after forming a bed of the soil (C).

The entire data with the soils have been given by the author elsewhere.* Here it will suffice to give only the correlations and general conclusions that resulted from this study.

*PURI, A. N., "Interaction between ammonia and soil as a new method of determining the state of saturation and pH values of soils," *Soil Sci.*, 33:397 (1932).

The relation between (V) and various sets of pH values is brought out best by working the correlation coefficients between them. These are given below:

(V) and (H) = 0.897
(V) and (Sb) = 0.891
(V) and (Q) = 0.889
(V) and (C) = 0.938

It will be seen that the correlations are highly significant. The difference is not very great, but with the colorimetric method slightly better correlation is obtained than with the other methods. From the correlations the following empirical formulas were determined for calculating the pH value from the known value of (V).

(1) pH = 0.0274 (V) + 5.4 for (V) values below 45%
(2) pH = 0.0319 (V) + 5.89 for (V) values between 45 and 81%
(3) pH = 0.0319 (V) + 7.11 for (V) values above 81%

A comparison of the calculated values with those determined by the H electrode or colorimetrically showed that the magnitude of the differences, except in the case of half a dozen soils, is not greater than what might be expected from the nature of such measurements, and is of the same order as differences between measurements of pH value by any two methods. The calculated pH values are, therefore, probably just as reliable as those obtained by any direct method. It might be mentioned that among the soils which show the greatest discrepancy are those which contain large proportions of humus. Soils with low T values are also likely to have considerable error in the determination of (V). In working out the correlations, soils having (V) values above 81% were left out, as these obviously fall in a separate group. Nor can it be expected that a linear relationship will hold good for the entire range, for that would mean that the titration curve of a soil is a straight line, which it is not.

Some very interesting facts emerge from a closer study of the (V) values for various soils. It was found that all soils having (V) values less than 33.3% respond to lime, the calculated pH value for which is 7. The neutral point, or pH 7, therefore, may have a more fundamental significance than has been hitherto supposed. Most of the good agricultural soils have (V) values between 50 and 70%. Soils having (V) value above 70% invariably contain sodium saloid, and those above 80% are all barren alkali soils. Soils that were in approximate equilibrium with $CaCO_3$ under field conditions gave values of about 62 to 68%. All soils having (V) values less than 40% are from humid regions where the rainfall is plentiful, and those above 70% (V) values are from arid regions.

CHAPTER IV

INTERACTION BETWEEN CARBONATES AND SOIL ACIDOIDS

If 33.3% saloid formation is taken as the basis of lime requirement, the ammonia method will give values comparable with the pH method of Hardy and Lewis* for the lime requirement of soils which consists in bringing the soil to pH 7. If on the other hand, the values of lime requirement are to be compared with the methods of Hutchinson or Kappen, which are equivalent to bringing the soil to pH 6.5, the lime requirement should be calculated to 25% of the (V) value. Hissink's method of determining (V) values gives the lime requirement as 28% of the degree of saturation, which is not very different. It must be emphasized that the various methods of finding the lime requirement of a soil merely represent different points on its titration curve, and unless the pH value of the suspension at the end of the reaction is defined, there can be no comparison between them. This has been the trouble ever since so many methods of finding the lime requirements of soil came into existence, many of which are still being practiced. Every such method is empirical and meaningless unless the pH value to which the soil acidoid is supposed to be neutralized is defined, or unless it bears a definite relation to the base equivalent of the acidoid.

If the limit of hydrolysis is taken as the equivalent point of the first hydrogen of the dibasic soil acidoid, we have yet another method for finding this point: namely, the interaction between soil acidoid and sparingly soluble $CaCO_3$. As we have pointed out, the main thing is to avoid excess alkali, which will carry the neutralization beyond the T/2 value. In the case of ammonia this has been accomplished by removing the excess in a simple and effective manner. The low solubility of $CaCO_3$, on the other hand, would serve the same purpose of automatically keeping the concentration of alkali low. In this case we can adopt either of the two procedures, i.e., either measure the CO_2 evolved as a result of the decomposition of $CaCO_3$ by soil acidoid, or determine the amount of Ca saloid formed as a result of neutralization of the acidoid.

The decomposition of $CaCO_3$ by soils was studied by Tacke as early as 1897. The reaction was allowed to proceed for three hours

*J. Agr. Sci., **19**:17 (1929).

and the CO_2 was expelled by a current of hydrogen and determined by absorption in standard $Ba(OH)_2$ solution. It was, however, recognized by the author that more CO_2 was given off when the mixture was heated, but he supposed the amount evolved in the cold to be the true measure of free humic acid in the soil.

Knight* modified Tacke's method for determining lime requirement of soils. He boiled the mixture of soil and precipitated $CaCO_3$ in the presence of a neutral salt (it made little difference what neutral salt was used as long as its percentage was not so high as to change the boiling point of the solution materially). Crowther† measured the interaction between $CaCO_3$ and acid soils in bottles completely filled with suspension, by measuring the total CO_2 liberated as free acid and as bicarbonate. The values thus obtained were found to be close to the amount of alkali required to bring the soil to pH 7.

On account of the limited solubility of $CaCO_3$, its reaction with soil acidoid has an attractive simplicity, for uniform conditions can be easily maintained for all soils, and no delicate adjustment is required for attaining the approximate equilibrium point. Besides, the mechanism of this reaction throws a good deal of light on the nature of soil colloids and on the properties of colloidal electrolytes in general. To understand the mechanism of the reaction, a few preliminary observations were made with buffer solutions of different pH values. Twenty-five cc of different buffers were mixed with 1 gram of $CaCO_3$ and the amount of CO_2 liberated was determined by passing it through a saturated baryta solution. A continuous stream of CO_2-free air was passed through the reaction vessel to insure complete removal of the liberated CO_2. It was observed that the decomposition of $CaCO_3$ can take place at all pH values on the acid side and that there is no correlation between the extent of decomposition and the pH of the buffer, the entire quantity of the acid being used up in every case. Thus it is the quantity of acid and not its strength that is important in determining the extent of the reaction.

The results with uric and stearic acid are interesting. With uric acid the reaction can be brought to completion even in the cold, although as expected it is extremely slow, requiring no less than a week for completion. In the case of stearic acid the amount decomposed in the cold is only 8% of the required value, which shows that stearic acid in the ordinary solid state has only 8% of active mass (this point will be referred to again). On heating we find that nearly 70% of the reaction is completed. This increase is obviously due to the increase in the total surface of the acid, since it becomes liquid at the boiling temperature. It is a remarkable fact that insoluble acidoids like soils, uric acid and stearic acid react with insoluble basoids like $CaCO_3$ to give insoluble saloids, and yet in each case the reaction tends to proceed to completion.

*J. *Ind. Eng. Chem.*, 12:560 (1920).
†*Agr. Progress*, Vol. II, (1925).

For experiments with soil acidoids, 10-gram portions of the various soils were mixed with 1 gram of $CaCO_3$ and 500 cc of water. The amount of CO_2 liberated was determined in the manner described above. When the reaction became extremely slow, the mixture was heated to boiling and the reaction continued in this way till it almost reached the end point. The results obtained before and after heating a few typical soil acidoids are given in Table 4.

Table 4. Interaction between H Soils and $CaCO_3$

Soil Acidoid		Milliequivalents per 100 grams		
		Amount of CO_2 liberated		/2 value (ammonia)
P.C. No.	pH	without heating	with heating	
6	3.82	12.4	11.2	11.0
13	3.65	43.6	48.1	48.0
73	5.05	12.9	26.4	17.2
86	4.38	23.3	16.5	20.8
110	5.00	14.4	14.1	10.6
121	4.48	19.5	11.9	14.8
122	4.50	12.4	11.7	8.8
152	3.98	20.7	15.1	13.9
209	3.70	18.2	15.1	16.0
214	4.35	11.9	13.2	13.0

It will be seen that the amount of CO_2 liberated by a soil without heating is nearly equal to its base equivalent as determined by neutralization with ammonia. The total amount of the gas liberated is nearly twice this value. No particular significance can be attached to this fact for the present. It is obvious that in the case of soil acidoid the reaction with $CaCO_3$ cannot be complete unless the CO_2 which would set up the back-reaction is removed from the sphere of reaction. Evidently this is not accomplished by merely passing a current of air; it is only on boiling that the CO_2 is completely removed.

If the soil acidoid is partly neutralized with NaOH, there is a regular decrease in the amount of carbonate decomposed and the decrease is almost equivalent to the amount of alkali added to the soil acidoid. In other words, the amount of carbonate decomposed is equivalent to the quantity of residual acidity contained in the partially neutralized acidoids.

Lime Status and Lime Requirement

The decomposition of $CaCO_3$ and measurement of the CO_2 evolved is a rather tedious business. We have at our disposal a much simpler method of achieving the same objective: namely, estimation of the Ca saloid produced by the interaction between $CaCO_3$ and soil acidoid. This method is based on the principle that Ca saloid, like any soluble Ca salt, is precipitated quantitatively by an oxalate. Thus when Ca saloid is shaken with a mixture of K oxalate and K carbonate so designed that the $CaCO_3$ is rendered completely

insoluble, the decrease in the concentration of the oxalate ion is equivalent to the Ca saloid present in the soil. A known weight of the soil acidoid is left, with excess $CaCO_3$ suspended in 50 cc of water. The suspension is occasionally shaken by hand for 2 or 3 hours, or may be left overnight. During this shaking the stopper is kept loose to allow the CO_2 to escape. The bottle can also be connected to an ordinary water pump and the reaction allowed to take place under reduced pressure when equilibrium can be attained in about half an hour. When the reaction is complete the suspension is cooled to 10°C and 50 cc of the following solution is added: 0.2N with respect to K oxalate, normal with respect to K acetate, 0.03N with respect to K carbonate.

The suspension is shaken by hand for almost half an hour while the temperature is kept round about 10°C. It is then filtered through a dry fluted filter, and 50 cc of the filtrate is titrated with standard permanganate. The total decrease in the concentration of the oxalate ion is equivalent to the Ca saloid present in the soil. In a similar manner we can determine the Ca saloid present in a natural soil without adding any $CaCO_3$. We can find the deficiency of calcium in the soil or its lime status (L.S.) as follows:

$$L.S. = \frac{100\ Ca_1}{Ca_2}$$

where Ca_1 is the Ca saloid in the original soil, and Ca_2 is calcium saloid after shaking with excess of $CaCO_3$. The lime requirement of a soil may be taken as equivalent to $(Ca_2 - Ca_1)$, i.e., the amount of Ca taken up from $CaCO_3$. We can express this value in tons per acre as follows: One acre (6 inches) weighs 2,000,000 pounds, which is equal to 1000 short tons. One milliequivalent of CaO is equal to 0.028 gram. Therefore an increase of 1 m.e. of Ca saloid per 100 grams of soil on shaking with $CaCO_3$ is equal to 0.28 ton of CaO per acre (6 inches). The lime requirement of a soil in tons per acre is therefore equal to $(Ca_2 - Ca_1) \times 0.28$. Of course this value has to be multiplied by a suitable factor according to the percentage of CaO in the given sample of lime. For instance, if liming is done with $CaCO_3$, lime requirement is equal to $(Ca_2 - Ca_1) \times 0.5$. It is interesting to note that the reaction between $CaCO_3$ and soil is very rapid; hence liming with $CaCO_3$ should be as effective as with $Ca(OH)_2$.

In Table 5 the lime status and lime requirements of some typical Indian soils are given. It is worthy of note that the results are not appreciably affected by changing the experimental conditions. No claim is made as to the application of these values to field conditions except in the case of soil 6, which was taken from a field the lime requirement of which was actually determined by the author by growing a crop on it and was found to be 1.43 short tons per acre. The value of 1.62 tons per acre found by this method is sufficiently close to justify field trials with other soils. At any rate the method

has the merit of simplicity and naturalness in the sense that even if lime is added to soil, the excess must be converted to $CaCO_3$, and it is the reaction with $CaCO_3$ that is of prime importance as far as the practical application of liming is concerned. Hitherto, this obviously simple method has not been tried to any extent because of the difficulty of finding the exact amount of $CaCO_3$ reacted with the soil acidoid. The measurement of CO_2 evolved is tedious and time-consuming. With the present technique as many as 50 soils could be examined in a day, if the laboratory is equipped with the requisite apparatus for routine work.

Table 5. Lime status and Lime requirement of Soils

Lab. No. P.C.	Locality	pH	Ca_1	Ca_2I	Ca_2II	Ca_2III	L.S. per cent	L.R. tons
3	Dharwar (Bombay)	7.64	51.2	52.0	52.4	55.6	98.5	0.22
6	Dacca (Bengal)	5.29	3.8	9.6	10.0	9.2	39.6	1.62
9	Malabar (Madras)	5.76	1.4	8.6	......	6.0	16.3	2.02
12	Tocklai (Assam)	5.84	2.8	7.6	8.2	6.8	36.8	1.34
14	Estate Soil (Madras)	5.37	6.8	17.0	18.6	15.0	38.6	2.86
15	Shillong (Assam)	7.71	11.6	15.6	15.0	14.4	74.3	1.12
20	Lower Burma	5.64	1.9	5.5	4.9	2.9	34.5	1.01
25	Bhin Soil (U.P.)	7.41	0.8	3.1	3.6	2.8	25.8	0.64
34	Gurdaspur (E. Punjab)	7.63	4.6	4.2	6.4	4.6	100	0
40	Umareth (Bombay)	7.65	7.6	9.6	10.4	8.8	79.2	0.56
45	Bihar	7.47	2.8	3.9	5.0	3.6	71.8	0.31
46	Baroda (Bombay)	7.63	38.2	43.2	42.2	......	88.4	1.41
49	Madhopur (Bihar)	6.33	10.8	13.6	15.6	13.6	79.4	0.78

Ca_1 = Ca Saloid in original soil (m.e. per 100 gm.)
Ca_2I = After treatment with $CaCO_3$ in water solution for 24 hours.
Ca_2II = After treatment with $CaCO_3$ in KCl solution for 24 hours.
Ca_2III = Ten minutes'shaking with water under reduced pressure.
L.S. and L.R. values on Ca_2I basis.
*Per acre 6 inches.

It is important that the distinction between lime status and lime requirement be clearly borne in mind. Lime status is a ratio, and as such can be used for comparing soils from different localities. It indicates the ratio between saloid and acidoid in a soil and shows how far the acidoid is already neutralized by bases. Its weak point is that it takes into account only Ca and possibly Mg. It is true that the amount of other saloids in normal agricultural soils is low compared to Ca saloid, but it is better to bear in mind exactly what is being measured than to be misled by a single value constant, merely because it measures something. Lime requirement, on the other hand, is a quantity that shows the deficiency of Ca in a particular soil and is not fundamentally related to lime status. In other words, two soils having the same lime status may have entirely different values for lime requirement. When the lime status of a soil is less than 100% we can say that it may require lime, but just how much per acre, we cannot tell. It is therefore advantageous when recording the values of lime status of soils to give the values for Ca_1 and

Ca_2 in milliequivalents per 100 grams of soil. This will enable anyone to calculate the lime requirement values if required.

The proposed method of finding the lime requirement of soils has the merit of simplicity and ease of manipulation. As it is based on a sound principle, the values obtained are not dependent on the amount of soil, the time of shaking, or the strength of solutions. The precautions to be observed are no more than those proposed for the analytical procedure for the estimation of Ca saloid. It must be pointed out that this ratio can have significance only when saloids other than those of Ca are absent, a condition rarely encountered in natural soils. A word of caution, therefore, must be given in connection with the interpretation of this constant when different soils are compared.

Lime status as a ratio also implies a straight-line relationship between the Ca saloid present in the soil and the maximum amount of Ca saloid that can form by the action of $CaCO_3$. This is correct only within a restricted range of pH, as can be seen from the titration curve of a soil acidoid with $CaCO_3$. (Figure 17).

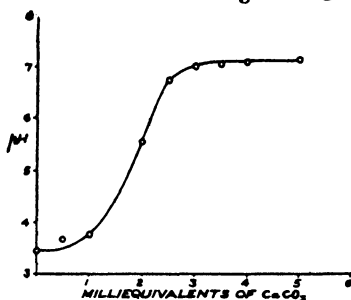



Fig. 17. Titration Curve of H-Soil with Calcium Carbonate

(Weight of soil = 5 gm.)

Incidentally the titration curve of a soil acidoid with $CaCO_3$ is another good method of finding its base equivalent. The only difficulty is that of weighing small amounts of $CaCO_3$ for incremental addition to the soil suspension. If a stable suspension of $CaCO_3$ could be made so that small amounts of it could be measured, it would reduce the time factor considerably. The beauty of the titration curve with $CaCO_3$ is that one can get a sharp break at the neutralization point; in fact the curve becomes horizontal to the X axis when the neutralization is complete. Any excess of $CaCO_3$ added beyond that point does not contribute to raising the pH value and therefore the values remain constant.

From the practical point of view much may be said in favor of the $CaCO_3$ equilibrium point as the basis for determining lime requirement of soils. The very slight solubility of $CaCO_3$ is a great advantage in maintaining uniform conditions which can be easily reproduced. It is necessary, however, to exercise judgment in the use of this method. It is evident that even soils requiring no lime

might show lime requirement if the method is used indiscriminately, without proper regard to the pH value of the soil and the presence of saloids other than those of Ca.

Comparison of Methods

We have so far discussed three methods of finding the base equivalent of soil acidoid, namely, the interpolation value from the titration curve (T/2); formation of ammonium saloid by the addition of excess of ammonia and removal of the excess by aeration or boiling; and the interaction of the acidoid with $CaCO_3$. We can now compare the three methods and at the same time find the final pH value of the soil acidoid when it is shaken with $CaCO_3$. For this purpose, 19 soils after the usual acid treatment and leaching were

Table 6. Calcium saloid formed in H soils shaken with $CaCO_3$

	one hour's shaking		48 hour's shaking			
Soil No. M Series	pH in equilibrium with $CaCO_3$	Ca Saloid m.e. per cent	pH in equilibrium with $CaCO_3$	Ca Saloid m.e. per cent	NH_3 taken up by 100 gm. soil	/2 per 100 gm. soil
1	7.12	25.2	6.78	24.4	24.4	23.2
2	7.28	13.2	6.86	16.0	11.6	12.0
3	7.24	15.2	6.79	13.6	13.4	14.6
4	7.29	13.2	6.78	14.4	11.4	12.8
5	7.18	22.8	6.76	21.6	18.6	20.0
6	7.30	10.8	6.90	9.2	9.2	10.0
7	7.25	17.2	6.81	16.8	13.6	28.0
8	7.20	26.8	6.74	25.2	26.2	28.2
9	7.31	8.4	6.99	7.2	8.8	12.4
10	7.20	21.6	6.90	20.0	20.4	16.6
11	7.33	18.0	6.93	14.0	13.0	14.0
12	7.24	19.2	6.88	19.6	19.8	16.2
13	7.37	8.4	6.97	9.2	9.6	9.4
14	7.26	14.8	6.93	15.2	10.6	10.6
16	7.43	7.6	7.00	8.8	6.2	5.8
17	7.32	8.4	6.92	10.4	13.6	10.0
21	7.25	15.2	7.04	14.8	22.6	14.2
22	7.34	9.2	7.01	13.6	12.0	12.3
23	7.28	12.0	6.95	10.0	14.4	12.5

shaken for 1 hour and also for 48 hours with excess $CaCO_3$; the final pH values were determined by the glass electrode; and the amount of Ca saloid formed was determined by the carbonate-oxalate method outlined above. The results are given in Table 6. The base equivalent values (T/2) determined by titration with NaOH and formation of ammonium saloid are also given.

It will be noted that 48 hours' shaking is not necessary to attain equilibrium with $CaCO_3$. There is no appreciable increase in the amount of calcium saloid formed when the suspension is shaken longer than 1 hour, though there is a slight fall in the pH values. The general agreement between T/2 values, the formation of ammonium saloid, and neutralization with $CaCO_3$, measured under en-

tirely different sets of conditions, would leave no doubt that we are dealing in all cases with reactions that are fundamentally identical. This can be reconciled only with the view that soil acidoids behave like true acids in their action on carbonates, ammonia and other alkalies.

It is evident that the pH value of soil in equilibrium with $CaCO_3$ is approximately equal to 7, in spite of the fact that a saturated solution of $CaCO_3$ has a pH value of 8.5. The fact that this value is reduced to 7 in the presence of Ca saloid is of great interest. It is evidently due to the lowering of the dissociation of $CaCO_3$ by the presence of a common ion, and the action is similar to that of soluble Ca salts. This will be seen from Figure 18 in which the pH values of a saturated solution of $CaCO_3$ in the presence of varying amounts of Ca and Na salts and soils are given. The influence of soil saloids is of the same order as that of acetates.

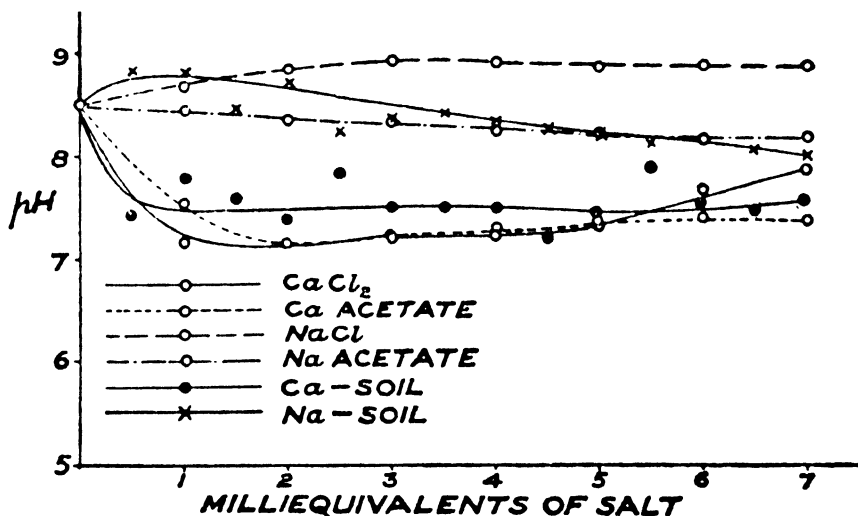



Fig. 18. Influence of Calcium and Sodium Salts and of Corresponding Soils on the pH Value of Calcium Carbonate Suspension

($CaCO_3$ = 5 m.e.)

As noted previously, the pH value of ammonium saloid is of the order of 8.2 as compared to 7 for Ca saloid, although both are chemically equivalent. Such differences in the case of soluble salts are of quite common occurrence, and the fact only emphasizes the general similarity of salts and saloids. The fact that the final pH value of Ca saloid lies at the neutral point, which is also the optimum for plant growth, gives added weight to this method for assessing the lime requirement of soils.

It remained to be seen whether a soil acidoid after being partly neutralized with $Ca(OH)_2$ or NaOH would take up the remaining portion of Ca to correspond to the equilibrium point. Increasing

amounts of $Ca(OH)_2$, $Mg(OH)_2$ and NaOH were added to a soil acidoid and the pH value of each mixture was determined after 48 hours' shaking. These suspensions were than shaken with excess $CaCO_3$, and the final pH value, as well as the Ca saloid formed, was determined in every case. The results are given in Table 7.

Table 7. Calcium saloid formed in H Soil first partly neutralized with NaOH, $Mg(OH)_2$, and $CA(OH)_2$ and then shaken with $CaCO_3$

	Sodium hydroxide			Magnesium hydroxide			Calcium hydroxide		
Amount of 0.1 alkal (CC)	pH	pH after shaking with $CaCO_3$	Ca saloid m.e. per 50 gm. soil	pH	pH after shaking with $CaCO_3$	Ca saloid m.e. per 50 gm. soil	pH	pH after shaking with $CaCO_3$	Ca Saloid m.e. per 50 gm. soil
0	3.46	7.15	32.2	3.46	7.15	32.2	3.46	7.15	32.2
5	4.53	7.20	30.0	3.65	7.09	22.8	3.58	7.10	33.6
10	4.49	7.34	26.5	4.07	7.15	20.8	3.86	7.13	33.0
20	6.40	7.66	14.6	4.63	7.19	17.0	4.58	7.18	32.6
25	7.68	7.88	8.6	6.10	7.30	12.0	5.97	7.26	32.2
30	9.08	8.54	3.6	7.24	7.56	6.8	6.94	7.36	33.0
35	9.68	9.04	1.2	7.80	7.62	3.6	7.50	7.33	34.2
40	10.20	9.80	0.6	7.97	7.68	3.0	8.58	8.28	39.4
50	10.87	10.34	0.4	8.25	7.78	1.6	9.14	8.82	40.6

Close examination of Table 7 reveals some interesting facts. When the soil acidoids are first neutralized with NaOH and then shaken with $CaCO_3$, the total amount of saloid, i.e., of Na+Ca remains the same, and the soil is able to take up small amounts of Ca even at pH 9.68. This is possibly due to the replacement of a certain amount of Na by Ca in accordance with the well known distribution of an acid between two bases, one of which is stronger than the other. The pH values of the soil saloids were determined before and after $CaCO_3$ treatment, and it is worthy of note that though the pH value of the Ca saloid alone is approximately 7, a mixture of Ca and Na saloid having the same equivalent weight has a much higher pH value. Therefore in the presence of Na saloid, in spite of the fact that the pH value may be even more than 9, the formation of Ca saloid can still take place. Of course part of this is due to the mutual saloid effect: the ionization of each is suppressed by the presence of the other, so that the total saloids at the equilibrium point are higher in the mixture than in the Na, Mg or Ca saloids individually.

Another noteworthy fact is that the estimation of Ca saloid can be carried out in the presence of Mg saloid. This would seem extraordinary, in view of the fact that Ca and Mg salts are generally precipitated together by oxalates. The reason for this separation in soils lies in the fact that the activity coefficient of a Ca saloid is very much higher than that of a Mg saloid; and in the presence of Ca saloid the ionization of Mg saloid is so completely suppressed that there are hardly any ions to react with potassium oxalate within the time prescribed for this reaction, i.e., 15 minutes. It will be

recalled that the application of the K_2CO_3-acetate-oxalate method for the estimation of Ca in Ca saloid, even in the presence of $CaCO_3$, is also based on the mutual saloid effect by which the ionization of $CaCO_3$ is completely suppressed, and thus no Ca ions from this source are available for precipitation by oxalate.

Lime Requirement Methods

It is convenient at this juncture to give a brief account of the empirical methods of finding lime requirement of soils, to which some reference has been made in the foregoing.

Lime requirement methods may be grouped under the following general heads:

(1) Reaction with neutral salts such as KNO_3 (Hopkins); KCl (Diakuhara also Kappen); $BaCl_2$ (Godroiz). The last named has suggested exhaustive treatment, others single treatment.

(2) Reaction with hydrolyzed salt such as sodium or potassium acetate (Loew); calcium acetate (Jones and also Kappen).

(3) Reaction with alkali such as $Ca(OH)_2$ (Veitch); $Ca(HCO_3)_2$ (Hutchinson and Maclennen); $Ba(OH)_2$ (Hissink, also Lyon and Bizzel, also Truog); neutralization to pH 7 (Hopkins).

(4) Reaction with ZnS and measurement of H_2S evolved. First suggested by Truog and later modified by Parker and Tidmore.

(5) Reaction with a carbonate and determination of CO_2 evolved; in the cold (Tacke), or on heating (Knight).

It is hardly worthwhile making a critical examination of the methods outlined above. Obviously they must give different points on the titration curve of the soil acidoid and therefore any comparison between them is a sheer waste of time. At one time they had attracted a good deal of attention, but the enthusiasm about them died down when it was realized that no two methods gave the same result. It is true that one or another of them is still used in soil laboratories for advisory work, but it is time that these empirical methods were discarded in favor of the titration curve which is the basis of all acidity measurement. We may still not be in a position to say which point on the titration curve would correspond to the lime requirement as understood by the farmer, but at least we know that by locating the exact point on the titration curve we shall know where we stand, and if our advice has miscarried we shall know exactly which side to turn to and not switch blindly from one method to another.

CHAPTER V

INTERACTION BETWEEN SULPHIDES AND SOIL ACIDOIDS

Falling in a somewhat similar category to the interaction between soil acidoids and carbonates is the decomposition of sulphides by acidoids. This reaction has been studied by Truog* but not strictly quantitively. In his field outfit Truog employs a mixture of $BaCl_2$ and ZnS which is heated with the soil suspension and the amount of H_2S liberated is indicated by the depth of color produced on a lead acetate test paper. According to this method it was found that the order of acidity noted for a number of soils was always the same as that determined by $BaCl_2$ replacement.

Parker and Tidmore† have suggested a modification of Truog's method, which consists in absorbing the H_2S evolved in dilute ammonia. An excess of standard iodine solution is then added, and the solution acidified with standard sodium thiosulphate of the same normality. They found that increasing the quantity of soil used in making the test increased the amount of H_2S evolved, but not proportionately. Increasing the quantity of reagent above 1.1 grams did not increase, but actually decreased the amount of H_2S evolved in some cases. The reaction is allowed to take place only for three minutes and other defined conditions must be adhered to rigidly to get reproducible results.

The main difficulty about this reaction is that water itself can hydrolyze sulphides, and a certain amount of H_2S is evolved purely for this reason; unless this is taken into account, it is impossible to study the extent of the decomposition brought about by the soil. Our methods of finding base equivalent of acidoids are much more refined and exact now than they were some years ago, and there is no reason why this reaction should not follow the general trend of results obtained in other reactions allied to it.

A number of preliminary experiments were performed to standardize working conditions, and the following observations furnished the basis for this standardization:

(a) The amount of H_2S evolved depends on the volume of water used.

*Wis. Agr. Expt. Sta. Bull. 49, 1915.
†*Soil Sci.*, 16:75 (1923).

(b) The reaction in the cold when completed can be pushed to another equilibrium point by heating.

(c) The reaction in the cold or on heating comes to a definite end point.

(d) The air passed into the reaction vessel to sweep out the H_2S should be free from CO_2.

The reaction vessel is a long-necked flask. CO_2-free air is passed when the reaction is allowed to take place in the cold. On heating, the water distills over, the steam carrying the H_2S evolved along with it and condensing into a standard iodine solution. Each time 250 cc of water (practically all of it) was allowed to distill over. After the first lot of water had distilled over, a second lot of 250 cc of CO_2-free water was added and the value thus obtained was taken as the blank which, when subtracted from the iodine reacted with the first lot, gave the true value of the decomposition brought about by the soil.

Potassium sulphide was used in the first instance with 5 soils; 0.5 gram of K_2S was used each time with 250 cc of water. The results given in Table 8 show that the base equivalent of the soil acidoid, as determined by neutralization with ammonia, is very nearly equivalent to the amount of H_2S evolved in the cold, and is also approximately equivalent to the amount of K taken up by the soil. The total amount of H_2S evolved on heating is only approximately equivalent to twice this value.

Table 8. Interaction between H soils and K_2S

Soil No. P.C.	H_2S liberated, m.e./100 gm. soil			T/2 m.e./100 gm. soil	K taken up m.e./100 gm. soil
	Without heating	After heating	Total		
13	60.2	35.4	95.6	58.6	54.0
122	9.1	13.1	22.2	8.8	8.2
123	25.0	35.6	60.6	25.3	24.2
138	10.3	6.5	16.8	7.6	8.1
155	12.6	12.2	24.8	11.8	11.5

A more comprehensive series of soils was then examined, using BaS instead of K_2S. The former has certain advantages over the latter on account of its limited solubility in water. Results with only 5 soils are recorded in Table 9 by way of illustration. Here again the total H_2S liberated appears to be nearly twice the base equivalent determined by neutralization with ammonia, and the agreement is closer in this case than with K_2S.

It has been shown that the reaction of the soil acidoid with ammonia represents approximately the neutralization of the first hydrogen of the dibasic acidoid (T/2 value). It would appear, therefore, that reaction with a sulphide on heating takes the acidoid to

the point of complete neutrality, and thus gives a true value of the base equivalent of the dibasic acidoid (T value).

That the H_2S liberated by the soil acidoid is equivalent to the base taken up by it can be shown in the following way. After reaction with K_2S in the cold the soil is leached with water till free from excess K_2S. It is then leached with 0.2N $(NH_4)_2CO_3$ to displace all the K that has reacted with the acidoid. The filtrate is evaporated to dryness, at which point all the ammonium carbonate is driven out, leaving behind the displaced K_2CO_3, which is equivalent to the K saloid formed by the interaction between the acidoid and K_2S. This is simply titrated with standard acid. These values are included in the last column of Table 9 and show very good agreement both with the base equivalent as well as H_2S liberated in the cold.

Table 9. Interaction between H Soils and BaS

Soil No. P.C.	H_2S liberated, m.e./100gm. soil			/2 m.e./100gm. soil	H_2S liberated by natural soil on heating m.e./100gm. soil
	Without heating	On heating	Total		
13	56.7	51.3	108.0	58.6	47.8
110	4.6	3.8	8.4	4.8	.....
122	13.4	6.4	19.8	8.8	.....
123	20.0	39.4	59.4	25.3	26.8
138	7.0	7.4	14.4	7.6	.....
168	6.5	7.0	13.5	6.0	.....
144	9.2	4.8	14.0	8.7	.....
154	14.0	11.0	25.0	10.5	10.2
155	13.2	11.6	24.8	11.8	.....

Soil acidoid partially neutralized with NaOH was next studied for decomposition of BaS. It was observed that there is a regular decrease in amount of BaS decomposed and that the decrease is almost equivalent to the amount of NaOH added to the acidoid. In other words, the amount of H_2S liberated is equivalent to the residual acidity of the partially neutralized acidoid.

It was stated earlier that natural soils subjected to a moderate amount of leaching tend to reach their limit of hydrolysis. It was also shown that this limit is attained when the dibasic soil acidoid is half neutralized (equivalent to T/2 value). It would appear, therefore, that a normal natural soil which is neither acidic nor alkaline will show very little decomposition of the sulphide in the cold. On heating, however, it may show a value equivalent to its T/2 value. This is brought out in Table 10, the values in which are comparable with those in Table 9. These results may be compared to the interaction between $CaCO_3$ and soils on heating. The parallelism is striking.

It is rather remarkable that although one would expect that the neutralization of the second hydrogen of the dibasic soil acidoid would take place in the presence of excess alkali at a high pH value

(and indeed this is actually the case with NaOH), this neutralization takes place by heating the acidoid with a sulphide or carbonate of Ba and Ca. The only explanation that appears to fit is that both BaS and $CaCO_3$ apparently yield a high concentration of hydroxyl ions at the boiling point of water, to complete the neutralization. It must also be remembered in this connection that the normal saloid formation of the acidoid will take place at a lower pH value with alkaline earths than with alkalies. Compare for instance the pH value of the ammonium H saloid with calcium H saloid (corresponding to T/2 value); in one case the pH value is of the order of 8.2 and in the other it is 7. This difference may be still greater when the normal saloid formation or the neutralization of the second hydro-

Table 10. pH Values of H soils determined by hydrolysis of ethyl acetate and inversion of sucrose

Serial No.	Clay (%)	pH of original soil	pH of H soil		
			Direct	Hydrolysis	Sugar inversion
1	32.2	7.32	3.18	3.24	3.28
2	20.6	7.64	3.67	3.80	3.96
3	8.7	7.64	3.67	3.75	4.06
4	11.5	7.92	3.67	3.55	3.52
5	16.0	8.14	4.92	3.80	3.82
6	13.9	7.90	3.57	3.68	3.54
7	29.8	7.50	3.08	3.22	3.28
8	9.3	7.61	3.42	3.68	4.02
9	25.3	6.94	3.44	3.22	3.42
10	11.3	8.48	4.26	3.62	3.92
11	21.8	9.59	5.31	4.22	4.36
12	22.4	7.85	4.66	4.08	4.10

gen takes place. It is also to be remembered that in the decomposition of both carbonates and sulphides it is the total acidity that is neutralized, and pH value as such has no influence. It is, therefore, reasonable to expect that the reaction will be pushed to the final stage of neutralization at the prevailing pH value.

There is evidence that complete neutralization of the soil acidoid with NaOH takes place in the neighborhood of pH 11.0, and it would not be surprising if in the case of $Ca(OH)_2$ or $Ba(OH)_2$ it is accomplished at 8.7, which may be achieved in a boiling solution of these alkalies.

CHAPTER VI

HYDROGEN ION ACTIVITY OF SOIL ACIDOIDS

We have seen that soil acidoids have a definite activity coefficient that can be expressed by their dissociation constants (K) or pK values, which can be measured with a fair degree of accuracy from their titration curves with NaOH. Besides the direct measurement of hydrogen-ion concentration electrometrically or colorimetrically, we have other methods of determining the catalytic activity of hydrogen ions in soil acidoids. The two best known ways to measure concentration of hydrogen ions by their catalytic activity are hydrolysis of ethyl acetate and inversion of sucrose. These are dealt with separately.

Hydrolysis of Ethyl Acetate

The relationship between pH value and hydrolysis of ethyl acetate is capable of being represented by a smooth curve. This will be clear from Figure 19, which gives the hydrolysis by buffer solutions of different pH values. The time of contact between the ester and the buffer solution was 24 hours at the ordinary room temperature (curve II) and 4 hours at 50°C (curve I). It is clear that virtually no hydrolysis occurs above pH 5. If we plot logarithms of the concentration of acetic acid produced against the corresponding pH value, we get straight lines. The relationship is therefore capable of being expressed mathematically, and the following formulas are obtained for the two temperatures:

Room temperature, 24 hours' shaking: $pH = 5 - 1.5 \log_{10} E$

At 50°C, 4 hours' shaking: $pH = 4.6 - 1.2 \log_{10} E$

where E is the amount of acetic acid produced in milliequivalents in both cases.

Temperature plays an important role in the rate of hydrolysis of ethyl acetate. There is practically no hydrolysis at 10°C because the rate is so slow that no appreciable amount of acetic acid is produced within a reasonable time of contact. The rate of hydrolysis rises very rapidly above 50°C and for all comparisons the temperature should be kept constant somewhere between 40 and 50°C.

As important as the effect of temperature is the influence of the concentration of ethyl acetate solution. In a study of this effect KCl–HCl buffer was used, both the strength of the buffer solution and the concentration of ethyl acetate being varied. The total volume of the buffer and ethyl acetate was 50 cc in every case, the mixture being kept for 25 hours at room temperature. If we plot logarithms of concentrations of acetic acid produced against pH values, series of straight lines are produced and the relationship can be expressed by the following formulas: pH = $2.5 \log_{10} \frac{C_e}{E}$, where C_e is the concentration of ethyl acetate, expressed in cubic

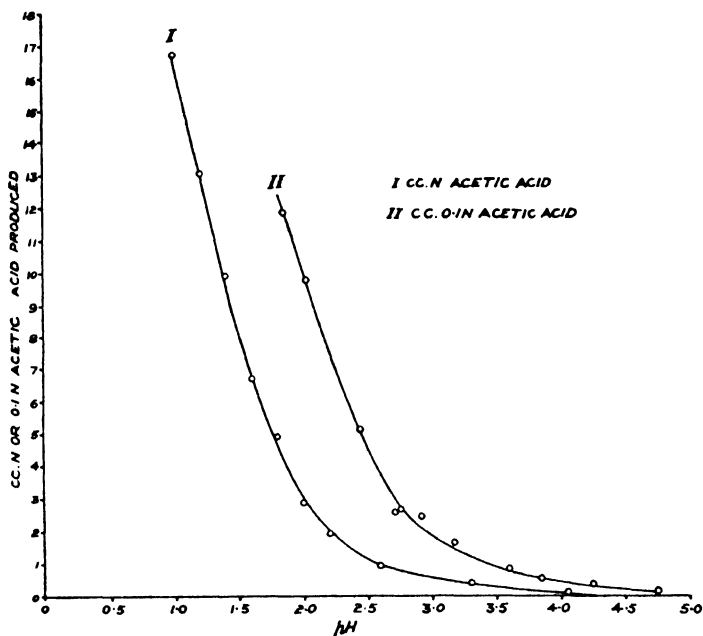



Fig. 19. Relation between pH Value and Hydrolysis of Ethyl Acetate

centimeters per 100 cc, and E is the amount of acetic acid produced expressed in cubic centimeters of 0.1N solution.

Since pH = $\log \frac{1}{C_h}$, where C_h is in the concentration of hydrogen ions, we have

$$\log \frac{1}{C_h} \cdot \frac{E}{C_e} = 2.5 \quad \text{or} \quad \frac{E}{C_e \cdot C_h} = 10^{2.5}$$

$$\text{i.e., } E = C_e \cdot C_h \times 10^{2.5}$$

which follows from the law of mass action, i.e., hydrolysis is proportional to the product of the active masses, which are the hydrogen ions and ethyl acetate in this case.

The effect of time of shaking, temperature and the concentration of ethyl acetate on hydrolysis in the case of soil acidoid is similar to that with buffer solution. These are shown in Figures 20 and 21. If the soil acidoid is gradually neutralized with NaOH by the addition of increasing amounts of alkali, it is seen that the first lot of alkali produces a great change in hydrolytic power, after which the change becomes more gradual until the hydrolytic power is completely lost.

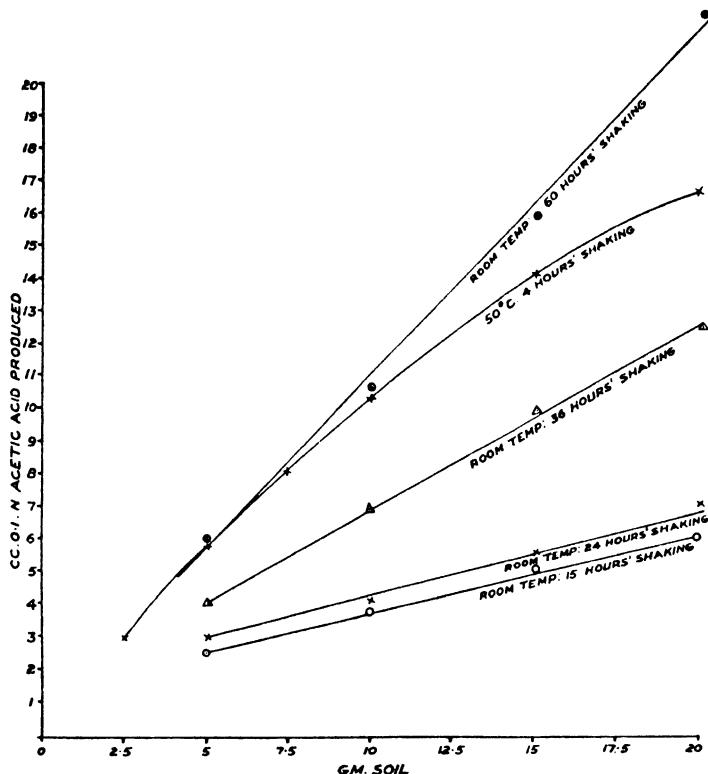



Fig. 20. Effect of Time of Shaking and of Quantity of Soil on the Hydrolysis of Ethyl Acetate

Because of the limited range of pH value in which hydrolysis is possible, as it ceases altogether at pH values about 4.75, the method is not suitable for finding the titration curves of soils. The results are interesting, however, in establishing the analogy between acidoids and true acids.

Sugar Inversion

The polarimetric method of determining inversion of sucrose is usually the best for mineral acids. Difficulties are experienced, however, in the use of the polarimetric method with soil acidoids. First, it is difficult to obtain a clear solution in many cases; secondly, the actual inversion is very small compared to the total con-

centration of the sugar solution, and consequently only a very small change occurs in the polarimetric reading, which is already very high. Titration of Fehling solution is free from these objections and can be successfully used for studying sugar inversion.

Standard Fehling solutions are made (a) by dissolving 69.28 grams of $CuSO_4$ to one liter, (b) by dissolving 350 grams of Rochelle salt (sodium potassium tartrate) and 120 grams of pure NaOH and making up to 1 liter. Five cc of each of the two solutions are mixed, diluted with about 30 cc of water, and gently boiled. The boiling

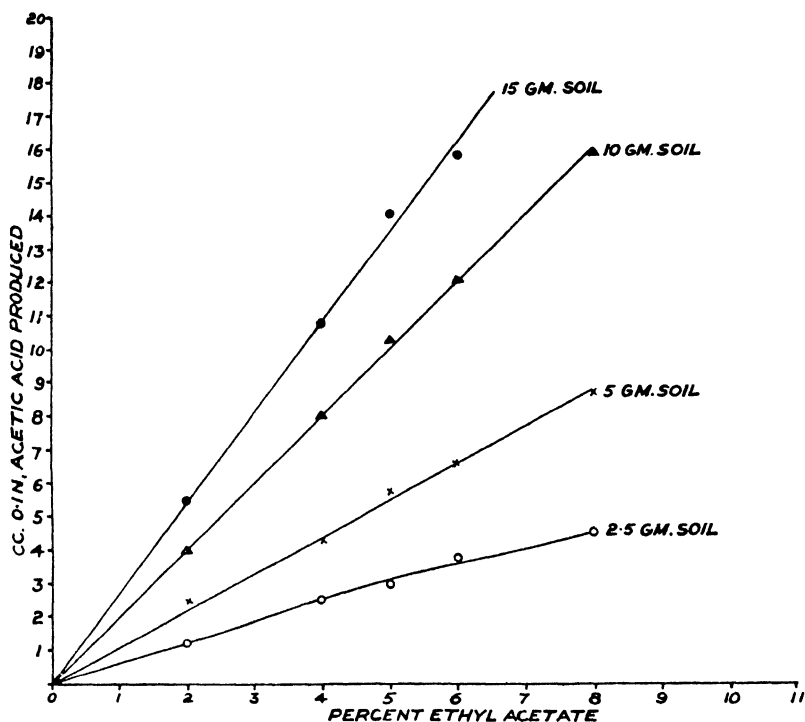



Fig. 21. Effect of Concentration of Ethyl Acetate on Hydrolysis by Soil

solution is then titrated with the sugar solution, care being taken that the glucose in the solution does not exceed 1%. Near the end point, which is determined by a preliminary rough titration, two drops of 1% methylene blue are added. Every time the Fehling solution is used it should be standardized with freshly prepared 1% glucose solution. As both glucose and fructose formed by inversion, better known as invert sugar, are capable of reducing Fehling solution, it is always the total invert sugar solution that is determined. A blank reading with sugar solution used is also taken every time to allow for the glucose in it. The general relation between pH value and sugar inversion is similar to that of hydrolysis with

ethyl acetate (Figure 22), and is defined by the following formula:

$$pH = 2.3 - \log_{10}E$$

where E is the sugar inversion in grams per 25 cc. This relation was obtained by using Na acetate-acetic acid buffers with four hours' shaking at 60°C.

Obviously the inversion of sugar, like the hydrolysis of ethyl acetate, depends on the concentration of sugar, the amount of soil acidoid, time of contact and the temperature. In all cases, however, the results can be expressed by smooth curves, so that for comparison all these factors can be arbitrarily fixed at convenient points when studying acidoids from different soils.

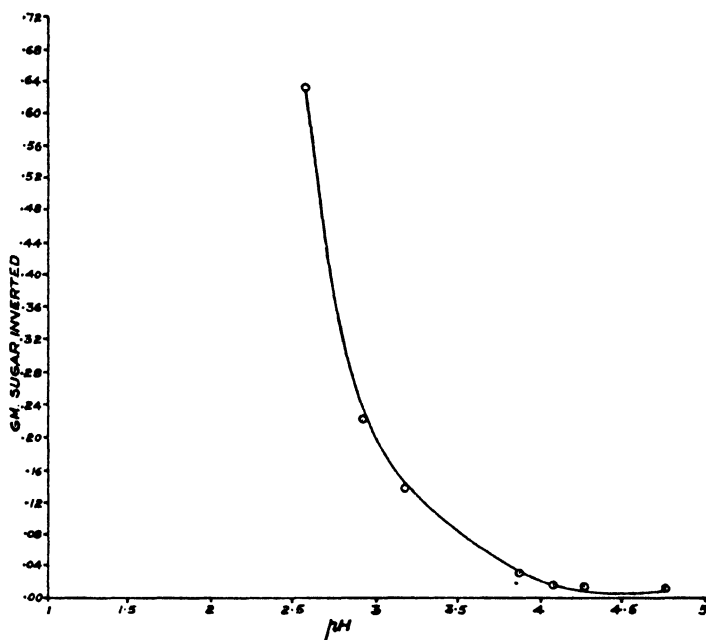



Fig. 22. Relation between pH Values and Sugar Inversion Na-Acetate-Acetic Acid Buffer, 4 Hours' Shaking at 60°C.

From a comparison of the relation between pH and hydrolysis as well as sugar inversion, it is seen that hydrolysis becomes inappreciable between pH 4.5 and 5, whereas sugar inversion stops somewhere about pH 5.5. It is worthy of note that both sugar inversion and hydrolysis continue to take place to a higher pH value in the case of soil acidoids than in the case of buffer solutions. This fact emphasizes the unreliability of the usual electrical methods of measuring the pH value of soil acidoids. This statement is likely to be misunderstood and therefore needs to be qualified. It should be noted that soil acidoid is not buffered, just as any weak soluble acid is not buffered until it is partially neutralized. The unrelia-

bility of the electrical method, therefore, mainly refers to soil acidoid in the absence of saloid; when present, the latter gives the mixture the characteristics of a buffer solution, which is not sensitive to slight alterations in the experimental conditions and lends itself to accurate measurement of pH value. It is also possible, and perhaps more probable, that the ionization of the acidoid, and consequently its pH value, is affected by the presence of ethyl acetate and sucrose, both of which might be expected to lower the pH value. Hence hydrolysis or inversion can occur even when the pH value of the acidoid-saloid in water is higher than the limiting value beyond which the catalytic activity of H ions ceases in the case of buffer solutions.

Table 11. Calculated and actual pH values of H soils in different salt solutions

Salts	P.C. 13		P.C. 146		P.C. 109	
	Found	Calc.	Found	Calc.	Found	Calc.
Potassium						
Chloride	2.7	......	2.8	......	3.4	......
Nitrate	2.7	2.7	2.8	2.8	3.3	3.4
Acetate	4.5	4.3	4.5	4.4	5.0	5.0
borate	7.2	7.1	7.5	7.2	8.3	7.8
sulphate	2.8	2.9	2.9	3.0	3.7	3.6
chromate	5.7	5.6	5.9	5.7	6.6	6.3
carbonate	7.3	7.7	7.5	7.8	9.3	8.4
Sodium						
chloride	3.0	......	2.9	......	4.0	......
sulphate	3.0	3.2	3.0	3.1	4.1	4.2
acetate	4.5	4.6	4.5	4.5	5.2	5.6
chromate	6.0	5.9	6.1	5.8	6.6	6.9
borate	7.4	7.5	7.5	7.4	8.3	8.5
carbonate	8.9	8.1	9.2	8.0	9.5	9.1
Ammonium						
chloride	2.6	......	2.7	......	......	......
sulphate	2.8	2.8	3.0	2.9	......	......
acetate	4.4	4.2	4.4	4.3	......	......
chromate	5.8	5.5	5.9	5.6	......	......
carbonate	7.7	7.7	7.9	7.8	......	......
Calcium						
chloride	2.5	......	2.6	......	3.4	......
sulphate	2.8	2.8	2.9	2.9	3.5	3.7
acetate	4.4	4.4	4.4	4.5	5.3	5.4
borate	7.9	7.9	8.1	8.0	8.7	8.8

From the general relation between pH value and hydrolysis of ethyl acetate as well as inversion of sucrose, the pH value of any soil acidoid could be determined by interpolation from either of the two relations. For hydrolysis 10-gram portions of soil acidoid may be shaken with 50 cc of 5% ethyl acetate solution for 4 hours at 50°C. Shaking may be done by hand at frequent intervals, after which the mixture is cooled and filtered, and an aliquot titrated with standard alkali. From the quantity of acetic acid produced, the pH

value is interpolated from the curve or calculated from the relation

$$pH = 4.6 - 1.2 \log_{10} E$$

where E is the amount of acetic acid produced in milliequivalents.

In the case of sugar inversion, 5 grams of the soil acidoid are kept in contact with 25 cc of 20% sugar solution at 60°C for 4 hours. The pH values can be calculated by the following formula:

$$pH = 2.3 - \log_{10} E$$

where E is the sugar inversion in grams per 25 cc.

These pH values of the soil acidoids are generally lower by 0.6 than those determined by hydrolysis. To obtain pH values of soils comparable with those determined by hydrolysis of ethyl acetate, therefore, 0.6 should be added to the interpolated values. It is a remarkable fact that this lowering of the pH value agrees with the observation of Moran and Lewis* and Corran and Lewis†, that sucrose is able to cause a large increase in the activity of various ions while not appreciably altering their concentration. The importance of these results is obvious insofar as they emphasize the essential similarity of acids and acidoids. In Table 11 are given interpolated pH values of soil acidoids by the two methods as well as direct determinations with the glass electrode. The pH value of the original soils as well as their clay contents are included in the table to show the diverse character of the soils. These values have been picked at random from a larger collection by way of illustration.

*J. Chem. Soc., **121**:1613 (1922).
†J. Am. Chem. Soc., **44**:1673 (1922).

CHAPTER VII

EXCHANGE ACIDITY

When a neutral salt is shaken with a soil acidoid, a portion of the cation of the salt is taken up and an equivalent amount of free acid is produced. This is one of the earliest observations of soil acidity. Similarly, when a hydrolyzed salt, i.e., a salt of a strong alkali and a weak acid, is shaken the amount of acid set free is considerably greater: it came to be known as the hydrolytic acidity of the soil. It is also referred to as potential acidity or exchangeable hydrogen. How this acid appears in solution, and how it is related to soil acidity has always been one of the greatest puzzles of soil science. The simplest explanation, based on "adsorption" and borrowed from colloid chemistry, appeared to be the handiest, and was almost universally accepted in one form or another.

It is well known that the distribution of a base between two acids is governed by the relative strength of the acids competing for the base, the stronger acid combining with the larger proportion of the base. In other words, if the relative amounts of the individual salts formed could be estimated, the relative strength of the acids in a mixture could be known. Similarly, as a salt is added to a soil acidoid, the amount of the basic portion of the salt going over to the soil acidoid will be governed by the relative strength of the acid radical of the salt as compared to the soil acidoid. For example, a larger proportion of the base would be taken up by the soil from acetates than from chlorides.

In the following discussion evidence will be presented to show that the whole phenomenon of exchange acidity is due to the distribution of a base between two acids, and is entirely governed by the relative strengths of the acid and the soil acidoid; it will be shown, moreover, that any special meaning attached to exchange or hydrolytic acidity or any distinction between the two is purely arbitrary and highly misleading.

One of the most accurate methods of following the distribution of a base between two acids is the measurement of pH values. When a mixture of equivalent amounts of two acids of unequal strength is titrated with a base, the titration curve is identical with that of the stronger acid at the start, and if the dissociation constants of the two acids differ greatly, almost all the stronger acid is neutralized

before the weaker acid is affected. From the nature of these titration curves it is possible to judge the relative strengths of the acids. On the other hand, the change in the pH value of an acidoid on the addition of an equivalent amount of a salt of an acid will indicate the strength of the acid.

The equivalent point of a soil acidoid can be determined from its titration curve, and is referred to as its T/2 value. Four soils of widely differing characteristics were used in the first instance after converting them into acidoids by treatment with 0.05N HCl as usual. Equivalent amounts of K salts of various acids were added to these soil acidoids and pH values determined with the glass electrode. When the pH values of the resulting mixtures are plotted against the logarithms of their dissociation constants, i.e., the pK values, a series of parallel lines for various soils is obtained.

Thus if the pH value of a soil acidoid in KCl solution is found, its pH value in any other solution of the K salt of the acid of which the pK value is known is given by the formula:

$$pH = 0.57\ (pK - 1.4)\ pH\ KCl \qquad (A)$$

It is, of course, understood that the various salts and the acidoid are used in equivalent amounts. The pK values of the various acids used are as follows:

Acetic acid	= 4.2	Carbonic acid	= 10.2
Chromic acid	= 6.4	Nitric acid	= 1.5
Boric acid	= 9.2	Sulphuric acid	= 1.8
		Hydrochloric acid	= 1.4

These acids in the concentrations developed in soils have no action on the electronegative portion of the soil acidoid. Formula (A) is applicable to K salts. For Na, NH_4 and Ca salts the following formulas were worked out from the straight-line relationships:

$$pH = 0.58\ (pK - 1.4)\ pH\ NaCl \qquad (B)$$
$$pH = 0.58\ (pK - 1.4)\ pH\ NH_4Cl \qquad (C)$$
$$pH = 0.69\ (pK - 1.4)\ pH\ CaCl_2 \qquad (D)$$

The calculated pH values for three soils in different salt solutions in comparison with those determined experimentally are given in Table 12 by way of illustration. In every case 5 grams of the soil acidoid was shaken for 48 hours with various salts in 100 cc of solution. The calculated and determined pH values show a good agreement for all types of soils studied (of which values for only 3 are given) and leave no doubt as to the nature of the exchange reactions involving the displacement of H ions.

The relation established in the foregoing is true only when equivalent amounts are used. It would be interesting to know how increasing amounts of salts affect the distribution of the base. From the titration curve of an acid, we can imagine any point on the curve as representing an acid which is weaker than the original acid. If we are dealing in terms of the H ions only, a series of acids of de-

creasing activity can be obtained by partially neutralizing any acid with increasing amounts of a base. For instance, the pK values of one-fourth, one-half, and three-fourths neutralized acetic acid are 4.7, 4.95 and 5.40, respectively.

We can regard an equivalent amount of any of these partially neutralized acids in the usual manner as containing 1 gram molecule of replaceable hydrogen. When they are neutralized the net result will be salts of increasing concentration. Alternately, we can regard increasing concentrations of a salt as the equivalent of a base neutralized with acids of decreasing activity. This conception may help us in visualizing the mechanism of pH changes of a soil acidoid with increasing amounts of salt. If we plot the pH values with

Table 12. Calculated and actual pH values of H soils in K acetate

Soil No. P.C.	pH with KCl	pH with K acetate		/2 values m.e./100gm.
		Found	Calc.	
2	3.0	4.6	4.6	55.0
6	3.4	4.8	5.0	12.0
7	4.4	5.5	6.0	8.2
15	3.8	5.1	5.4	5.1
32	3.3	4.9	4.9	58.5
68	4.1	5.4	5.7	18.2
70	3.6	5.4	5.2	48.0
73	3.6	4.9	5.2	28.3
110	4.1	5.4	5.7	10.1
114	3.6	5.5	5.2	40.5
115	3.9	5.6	5.5	30.2
116	3.9	5.3	5.5	19.0
122	3.8	5.3	5.4	8.1
124	3.5	5.1	5.1	15.0
132	3.2	5.0	4.8	18.2
138	3.8	5.0	5.4	10.3
152	3.6	5.2	5.2	36.4
153	3.8	5.5	5.4	44.0

different concentrations of a salt against the calculated pK values, the results fall on straight lines characteristic of different acids. HCl being completely ionized, the same pH is obtained at all concentrations with KCl, which fixes the starting point. The formulas developed can be used for finding the pH value of a soil acidoid in any solution at any concentration, provided we know the pH on the addition of an equivalent amount of the salt from formulas (A) to (D). The equation giving the relation between pH and pK values at different concentrations is described as follows:

Equations (A) to (D) can be written in the general form:

$$pH = m\,(pK - pK_0)\,pH_0 \qquad (E)$$

in which pH_0 is the pH value when the soil is treated with KCl at equivalent concentrations; pK_0 is the dissociation constant of HCl (= 1.4); pK is the dissociation constant of the acid of which the salt is used, and m is the slope of the line. For the equation of any

straight line that branches off from this line at any point (i.e., the line showing the relation between concentration and pH), the equation will be:

$$pH_1 = m_1 (pK_1 - pK) + pH \qquad (F)$$

in which pH is the value when the concentration of the salt is equivalent to that of soil acidoid and which is given by formula (E), i.e., pK is the dissociation constant of the acid in accordance with the assumption made above; and m_1 is the slope of the line showing the effect of concentration on pH.

Substituting numerical values in equation (F) in the case of soil P.C. 13 acidoid we have for acetates:

$$pH_1 = 0.835 (pK_1 - 4.2) + 4.3$$

and for borates:

$$pH_1 = 1.72 (pK_1 - 9.2) + 7.3$$

The values of pK_1 are of course calculated for every concentration in accordance with the assumption that a higher concentration of salt may be taken as the salt of a weaker acid.

The following relation is used for finding the pK value. If C_1 is the concentration of the salt and C_2 is the concentration equivalent to the soil acidoid, then the pK_1 value of the partially neutralized acid equivalent to the soil acidoid is given by the pH of the acid neutralized to $100 (1 - \frac{C_2}{C_1})$ %. This value is interpolated from the titration curve of the acid. An example will make this point clear. Suppose we want to find the pH value of a solution containing 10 m.e. of K acetate when shaken with a soil containing 2 m.e. of acidoid. The pK_1 value of the partially neutralized acid will be equal to pH when $100 (1 - \frac{2}{2 \times 10}) = 90\%$ of acetic acid is neutralized with KOH. From the titration curve of acetic acid this is found to be 5.6. Substituting this value in formula (F) we have:

$$pH_1 = 0.835 (5.6 - 4.2) + 4.3 = 5.46$$

When dealing with salts of dibasic acids like chromic and carbonic, a straight-line relation does not occur at low concentrations. The reason is obvious. These acids have a point of inflection at the end of the first half of the neutralization when the conditions are highly unbuffered, and therefore a slight change in the degree of neutralization can produce a large difference in the pH value. The measurement of the pH value is not reliable in this region, and it is not certain whether we are dealing with the first or the second dissociation constant unless we work with concentrations so high that they can fall only in the second half of the titration curve. Sulphates, on the other hand, fall in line with salts of a monovalent acid, because

there is no point of inflection at the end of the first half of the neutralization.

The data presented in the foregoing should leave no doubt as to the fundamental cause of the so-called exchange acidity which is governed by the law of distribution of a base between two acids of unequal strength. The fact that one of the two acids is an acidoid does not make the slightest difference in the state of equilibrium or its mathematical treatment.

CHAPTER VIII

HEAT OF NEUTRALIZATION OF SOIL ACIDOIDS

It is well known that the process of neutralization of any strong acid in dilute solution consists in the union of the hydrogen ion of the acid with the hydroxyl ion of the base, forming a molecule of water. The process of neutralization is the same for any acid or base which dissociates completely. If the acid or base is weak and only partially dissociated by water, neutralization can proceed only until all the undissociated molecules have dissociated. The accompanying thermal change, if positive, is added to the heat of neutralization, and if negative, diminishes it. There is no independent evidence to show the negative or positive heat of dissociation, however. As a matter of fact, in no case is there a positive heat of dissociation, and therefore the heat of neutralization never exceeds the heat of combination of hydrogen and hydroxyl ions in the case of weak acids or bases, which are expected to undergo progressive dissociation or neutralization.

It is clear that the heat of neutralization of acids and acidoids with a particular base is a function of its dissociation constant: the stronger the acid the greater the heat of neutralization. Consequently, if we neutralize an acid progressively and measure the heat of neutralization and plot the results against the incremental additions of alkali, we get a curve similar to the familiar titration curve, with a point of inflection at the neutral point. Such curves for a number of acids as well as the soil acidoid are shown in Figure 23.

The heat evolved in every case is a function of the pH value, so that over the buffer range of the acid, the heat of neutralization for every addition of alkali changes but little. There is an abrupt drop in the heat of neutralization toward the end point, when the pH value rises rapidly. Results with phosphoric acid are interesting. The three stages of neutralization corresponding to the di-acid, mono-acid and normal salt formation are shown in the curve. The general similarity of the soil curve to those of the common acids leaves no doubt that the fundamental reaction is the same in all cases.

Heats of neutralization can be measured in a Dewar cylinder about 4 or 5 cm in diameter fitted with a stirrer and a Beckmann thermometer capable of reading to 0.002°C. Two such cylinders

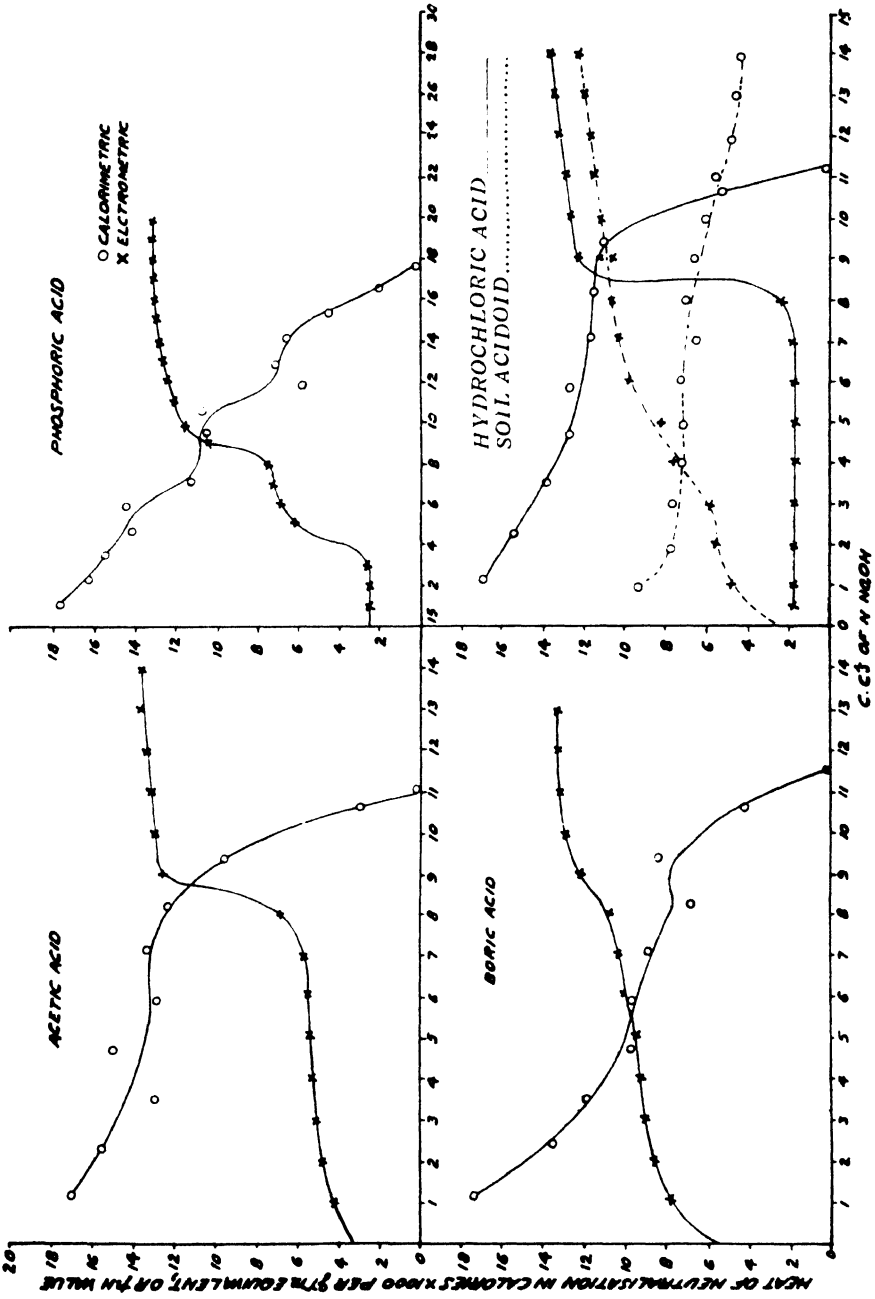



Fig. 23. Calorimetric and Electrometric Titration Curves of Acids and Soil Acidoid

should be used, one for holding the acid and the other for the alkali solution. The latter is added with a pipette which is waxed on the outside to reduce to absolute minimum the thermal change during transference. A known weight of the soil acidoid is suspended in a known volume of water and the temperature noted. A known volume of alkali solution, the temperature of which is also known, is added to the suspension and the rise of temperature noted; from these data the heat of neutralization per gram equivalent of alkali is computed. All the results are recorded in calories per gram equivalent of alkali.

It is worth emphasizing that to get the best results in studying the heat of neutralization of soil acidoids, they should be completely dispersed in water. This is done simply by converting the acidoid

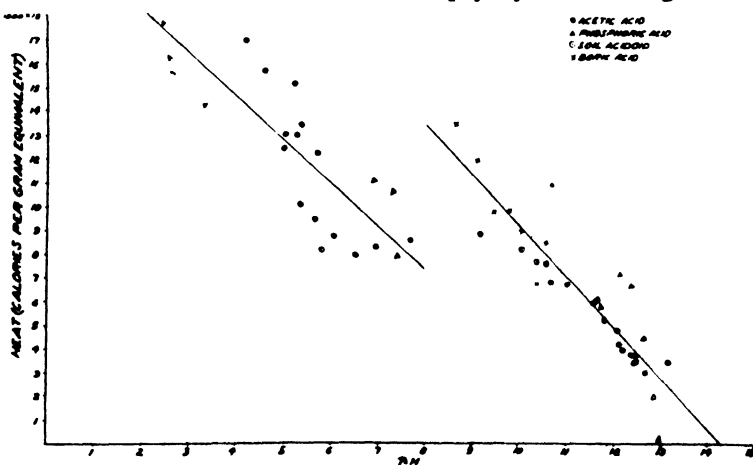



Fig. 24. Relation between pH Value and Heat of Neutralization

into sodium saloid and then reconverting it to the acidoid without allowing it to dry. The full significance of these steps will be explained later.

If the heats of neutralization per gram equivalent of alkali for various acids at different stages of neutralization are plotted against the corresponding pH values obtained from their electrometric titration curves, two straight lines result, one for the acid range and the other for the alkaline range. (Figure 24).

The relation between pH and heat of neutralization (H) for acid and alkaline ranges derived by fitting a straight line to the data by the method of least squares, is as follows:

$$\text{For acid range: } H = 21.34 - 1.73 \text{ pH}$$
$$\text{For alkaline range: } H = 30.22 - 2.11 \text{ pH}$$

The linear correlation coefficients are 0.84 and 0.91, respectively, both values being highly significant.

In working out these relations the values for soil acidoid have been included along with those of other acidoids, and the various points pertaining to soil are in no way distinct from other common acids; this is additional evidence that soil acidoids behave just like other acids as regards heat of neutralization.

CHAPTER IX

RELATION BETWEEN SPECIFIC SURFACE AND CHEMICAL REACTION

Particle Size and Specific Surface

The surface reaction of soils has led some workers to postulate the existence of a colloidal coating on the soil particles. How this hypothetical coating is bound to the particles is not explained. It is also not clear why this coating does not wear off, for soils in nature are subject to several forces of attrition which would remove any colloidal coating in a short time. A much more logical way of regarding the colloidal behavior of soils would be to suppose the existence of particles of colloidal dimensions. That such particles do exist can be demonstrated by ultra-mechanical analysis of soils, to be described in another chapter. That so far they had escaped attention is due to the fact that the lower limit of particle size in the usual method of mechanical analysis has been 0.002 mm or 0.001 mm at the most. These would be considered very coarse compared to colloidal dimensions.

Specific surface is defined as the surface area per unit mass of the particles. Since chemical reactivity is confined to the molecules constituting the surface, we may define as "active mass" that portion of the total weight which constitutes the monomolecular surface layer. When active mass constitutes an appreciable percentage of the total mass of a substance, it is said to be in the colloidal state. This definition of the colloidal state, as we shall presently see, is preferable to others of a more or less conventional type.

The active mass of a substance can be calculated from its specific surface and from the diameter of the molecules constituting the surface in one gram of the substance. This value when divided by N (Avogadro's number) gives the active mass in gram molecules per gram of the substance. If this value is multiplied by the molecular weight of the substance we get the active mass in gram molecules per gram molecule of the substance, which can be expressed as a percentage by multiplying by 100. Thus the active mass of a substance increases from zero to 100% when the coarse particles are gradually reduced to a state of molecular dispersion. The colloidal state is the intermediate state in which the increasing degree of dispersion is associated with increasing percentages of the active mass.

Specific surface is given by the formula:*

$$SS = 0.02264 \sum p/d$$

where p is the percentage by weight of particles of mean diameter d. It is evident that the value of specific surface would vary with the point at which analysis is stopped; it is thus not possible to get its unique value unless it is with reference to some fixed lower limits of analysis. The following numerical example will make this point clear. A soil has the following percentages of particles of different sizes:

Percentage	of	particles	below	0.002 mm	58.8
"	"	"	"	0.001 mm	57.8
"	"	"	"	0.00063 mm	54.6
"	"	"	"	0.00004 mm	26.4

If the analysis were stopped at 0.002 mm, the contribution of the particles below this size to the specific surface would be

$$S_1 = 0.002264 \frac{58.8}{\frac{1}{2} \times \frac{.002}{10}} = 1.33 \text{ sq. m. per gram.}$$

(The diameter of the particles of the lowest size is taken to be equal to half that of the finest particles determined by analysis). Similarly, if the analysis is stopped at 0.001 mm the contribution would be:

$$S_2 = \frac{58.5 - 57.8}{\frac{0.0015}{10}} + \frac{57.8}{\frac{1}{2} \times \frac{0.001}{10}} = 2.63 \text{ sq. m. per gram.}$$

If the analysis is stopped at 0.00063 mm and 0.00004 mm the contributions are S_3 and S_4, respectively:

$$S_3 = 4.04 \text{ sq. m. per gram}$$
$$S_4 = 31.8 \text{ sq. m. per gram.}$$

It appears, therefore, that specific surface must be defined with reference to the lower limit of analysis, and the accuracy of determination of its active mass or chemical reactivity will depend on the lower limit, which may be taken as 0.00004 mm, or $10^{-5.4}$ cm. The following empirical formula also can be used to determine the specific surface of soils when the percentage of particles below 0.00004 mm (= p) is known:

$$SS = (13.51 \times p + 17.4) \times 10^3$$

This relation affords a convenient method of estimating the specific surface of soils by determining the percentage of particles of 0.0004 mm diameter with the help of refined pipette technique for the ultramechanical analysis described later. Specific surfaces of a few typical soils calculated directly from ultramechanical analysis

*The derivation of this formula will be discussed in another chapter.

and from the percentage of particles of 0.00004 mm diameter are given in Table 13. It will be seen from these data that the values of specific surface for some of the soils are of a much higher order than those given by previous workers.

Hitherto we have confined ourselves to particles of diameter $10^{-5.4}$ cm as the smallest size for calculating specific surface, because this could be determined experimentally by the pipette method. There is, however, no reason why there should not be particles smaller than that. As a matter of fact the general trend of the summation curves lends support to the contention that we are dealing with much smaller particles; we should choose the smallest size for the specific surface, and for this purpose particles corresponding to $10^{-6.5}$ cm diameter seem quite appropriate. These can be determined by interpolation from the mechanical analysis summation curve, which is supposed to originate at 10^{-7} cm diameter, or about the size of molecules. In Table 13 are included values for specific surface obtained by taking the limiting size of particles as $10^{-6.5}$ cm. Results are recorded to the nearest square meter.

Table 13. Specific surface of soils by various methods

Soil No. P.C.	Sp. surface (sq. meters per gm.)				Base equivalent (m.e./100gm. soil	
	Limiting size $10^{-5.4}$cm.		Limiting size $10^{-6.5}$cm.			
	Determined Size distr.	Calculated Emp. formula	Determined interpolation	Calculated M. absorption	Calculated	Found
2	37	38	151	238	119	108.8
3	46	49	194	233	116.5	122.0
4	4	5	16	28	14	12.6
5	4	4	16	18	9	21.1
8	22	25	102	72	36	39.2
9	12	12	38	37	18.5	15.4
10	28	28	110	98	49	39.6
11	26	28	111	108	54	52.0
12	6	6	22	12	6	11.0
13	37	38	180	206	103	90.0

It is evident that there is a vast difference between the values of specific surface calculated from particles of $10^{-5.4}$ cm diameter as the lowest limit and those calculated from $10^{-6.5}$. The latter values are 3 to 4 times as great as the former. They are, however, more reliable in view of the fact that the summation curves do not end abruptly.

There is yet another method of determining the specific surface, i.e., from the vapor-pressure curves. This will be discussed later. The values obtained by this method are, in some cases, even higher than those determined by mechanical analysis up to the limiting size of $10^{-6.5}$. These values are included in Table 13.

We have seen that the total surface exposed by soils is enormous, far exceeding the highest value ever calculated before, which was only a fraction of a square meter per gram of soil. This was, of course, due to the fact that mechanical analysis was stopped at

0.002 mm, or 0.001 mm diameter at the most. The contribution of this size toward the total specific surface in soils is hardly more than 1 to 2 per cent. We can in fact completely ignore particles of 0.002 mm diameter (our so-called clay) without making any appreciable difference in the specific surface. When it is remembered that this is the lowest size determined in mechanical analysis it is plain that we have not touched even the fringe of chemical reactivity.

Now that we have a fair idea of the total surface exposed in typical soils, let us see the amount of active mass they contain. If the chemical reactivity of a soil is due to the ferroaluminosilicates, we can ascertain the mass of the silicate molecules constituting the entire surface of the soil acidoid as follows:

If we assume two molecules of aluminum silicate linked with one molecule of water in a long chain, we shall have the diameter of the silicate complex equal to $(0.23 \times 2 + 0.345) \times 10^{-7}$ cm, with the hydrated part exposed on the surface, giving it the character of a dibasic acid. The number of active silicate molecules occupying a surface of one square meter in a monomolecular layer will be

$$\frac{10^4}{(0.805 \times 10^{-7})^2} = \frac{10^4}{0.648 \times 10^{-14}} = 1.54 \times 10^{18}$$

The number of molecules in a gram molecule being 6.02×10^{23} we have

$$\frac{1.54 \times 10^{18}}{6.02 \times 10^{23}} = 0.25 \times 10^{-5} \text{ gm. mols.}$$

of acidoid for every square meter of the surface. Since silicic acid is dibasic, the surface acidity is equal to 0.5×10^{-5} gram equivalent per square meter of surface. Or, expressing the acidoid content in general terms, the active mass or surface reactivity of a soil is equal to $(0.5 \times 10^{-5} \times 100 \times 1000)\ S = 0.5S$ milliequivalent per 100 grams, where S is the specific surface in square meters per gram.

The correctness of the above hypothesis can be easily tested by determining the specific surface of a set of soils and also finding their base equivalent from the titration curves, or by any other method previously outlined. Such values as those given in Table 13 leave no doubt that the basic idea underlying the theory is sound. The calculated values of base equivalent refer to specific surface calculated from moisture absorption at various humidities. As will be explained later, these are the most reliable values of specific surface, as in the other case the percentage of particles of $10^{-6.5}$ cm diameter is determined by interpolations from the summation curves; and the values are not as reliable as in the case of moisture absorption. However, the two sets of values probably represent the limits within which the true value of specific surface lies, and the determined base equivalent values are in some cases nearer one than the other.

The relation between active mass and specific surface is of general application. The only uncertainty lies in the diameter of the

silicate molecule, which is not likely to be greater than the value taken; the calculated values for base equivalent therefore are the least possible. For oriented long-chain molecules like stearic and palmitic acids, in which H ions alone may be exposed to the surface, the active mass per unit surface may be much more. We can work out the active mass as a percentage of the total weight as a function of the particle size as follows. If we accept the formula of aluminum silicate as $[Al(OH)_3]_2Si_2O_5$, then its molecular weight is 258. In other words, one gram of the silicate complex will contain 1/258 gram molecules. If s is the specific surface the active mass is $(258 \times s \times 0.25 \times 10^{-5} \times 100)$ % of the total mass = $(S \times 64.5 \times 10^{-3})$ %. Now $S = 0.02264 \times \frac{100}{d} = \frac{2.264}{d}$ sq. cm. or $\frac{2.264}{d} \times 10^{-4}$ sq. m. Thus the active mass in terms of the diameter of particles is $\frac{2.264 \times 10^{-4}}{d} \times 64.5 \times 10^{-3}$ gram molecules per gram, or $\frac{2.264}{d} \times 64.5 \times 10^{-7}$ gram molecules per gram. Thus the active mass corresponding to particles of different sizes can be calculated; such values are given in Table 14.

Table 14. Relation between size, specific surface and "active mass" in soils

Size pD*	Sp. surface (sq. meter per gm.)	Active Mass		
		per cent	m. mols. per 100 gms.	milliequivalents per 100 gms.
7	2264	146 (100)	566	1132
6.75	1260	81.5	315	630
6.5	704	46.0	176	352
6.25	400	26.0	100	200
6.0	226.4	14.6	56.6	113.2
5.75	126	8.15	31.5	63
5.5	70.4	4.60	17.6	35.2
5.25	40.0	2.60	10.00	20.0
5.0	22.64	1.46	5.66	11.32
4.75	12.6	0.815	1.76	3.52
4.5	7.04	0.460	1.00	2.0
4.25	4.0	0.260	0.566	1.32
4.0	2.264	0.146	0.315	0.63
3.75	1.26	0.0815	0.176	0.352
3.5	0.704	0.046	0.100	0.200
3.25	0.40	0.0262	0.0566	0.1132
3.0	0.2264	0.0146	0.0315	0.063

*pD is the negative index of diameter of particles in centimeters.

It is remarkable that when the particle size is of the order of 10^{-7} cm, the active mass has already reached 100%. This is easily understood when it is remembered that the size of the silicate complex has been assumed to be of the order of 0.805×10^{-7}. Of course the calculated value of 146% for the active mass is fallacious and merely indicates that the active mass becomes 100% before the particles are reduced to the monomolecular state. This is not sur-

prising when it is remembered that we can have an aggregate of eight spheres in which each sphere will be exposed, giving 100% active mass.

The values in Table 14 (columns 1 and 2) can be plotted to give a smooth curve from which any intermediate value can be interpolated. (Figure 25).

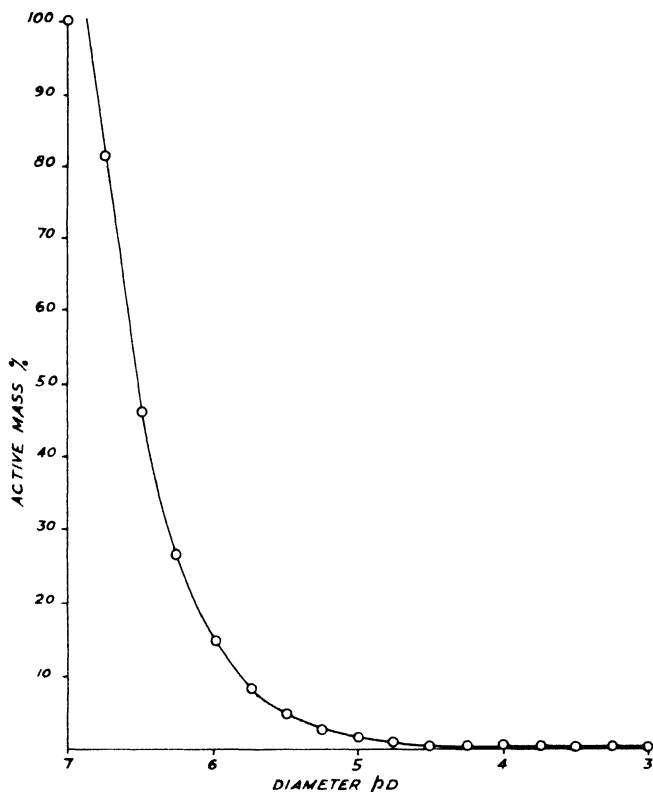



Fig. 25. Relation between Diameter of Particles and Active Mass

Colloidal Considerations

Since the active mass in this case is given in percentages of the total mass, irrespective of the size of molecules, which in any case would make very little difference for ordinary molecules, these values are applicable to all colloidal solutions. It will be noticed that even coarse suspensions (diameter 0.01 mm = pD 3) have an active mass which might be measured by ordinary analytical methods. Thus if 100 grams of these particles (which would be classed as silt in soil nomenclature) were suspended in 100 cc of water the suspension would appear to be a 0.0146% solution of some weak electrolyte. This suspension will have a conductivity appreciably higher than that of water; its reaction will be weakly acid and it will require approximately 0.66 cc of 0.1N alkali to neutralize that

acidity. This will be multiplied ten times in the case of particles of 0.001 mm diameter. Still such a suspension is regarded as coarse and outside the domain of colloidal solution; it may even precipitate in a day or two, depending upon the depth of the container. When we come to particles of 0.0001 mm diameter we are really getting down to what is known as the colloidal state, but we have still a long way to go before entering the domain of molecular solutions. Already little over 0.6% of the substance is as good as in a molecular solution – a two-dimensional solution which has area, but no depth; but it must behave exactly like any other molecular solution. If the substance is an acidoid or a basoid, it must give a measurable concentration of hydrogen and hydroxyl ions depending upon the dissociation constant. It must exhibit all the characteristic reactions of an acid or a base, not merely qualitatively but quantitatively, exactly as if that portion of the substance which constitutes the surface was in true molecular solution.

Solubility and insolubility are relative terms. A substance is soluble in water when its molecules have so much attraction for water that it can overcome the cohesive forces that bind the particles together. However, it is conceivable that we may be able to overcome these cohesive forces by some other means and reduce the substance to the molecular state. In that case the substance will be as good as in solution. We can also imagine that even if it is difficult to reduce a substance to the molecular state it would not be at all difficult to stop short of that state, in which case only that portion of the substance will be in solution which is in contact with water molecules; i.e., that portion which constitutes the surface, which we have called the active mass, will be as much in true solution as any common molecular solution. If we accept this view, the entire range of colloid chemistry falls into natural alignment with classical chemistry and atomic theory: there is no necessity of introducing adsorption. We never talk of hydrochloric acid having adsorbed Na to give NaCl; nor do we call it a case of base exchange when exchangeable H has been replaced by Na. We call it a straightforward chemical reaction, which takes place because the reacting substances are in molecular solution; that is the main criterion.

Every colloidal substance presents an enormous surface in contact with water, which may be supposed to be in solution. This portion, being in solution, is chemically reactive. We can thus replace the entire colloidal solution by that portion of it which constitutes the surface, or the active mass.

It is true that every colloidal solution does not consist of acids and bases which can be easily determined; but irrespective of the nature of the salt, if we accept the view that the surface molecules are in true solution, most of the phenomena associated with colloidal solutions become conceivable. We have hitherto made the mistake of considering the colloidal solution as a whole. While this may be

all right in considering some of their physical properties, there is no justification for its introduction in the chemistry of colloids. Every colloidal solution can be replaced by a molecular solution of its active mass; the need for adsorption, sorption, and chemisorption disappears, and we are face to face with the atoms and molecules of classical chemistry – familiar objects with their well established laws of chemical equilibrium.

A colloidal solution should not be regarded as a heterogeneous system, but as a homogeneous, molecular solution of its surface molecules. For all practical purposes while considering its chemical reactions we can disregard the molecules that do not constitute the surface, and which are not in contact with water. They constitute the inert mass, as opposed to the active mass. This inert mass is not in equilibrium with the active mass. The relation between the two is not dynamic but static, and when a portion or all of the active mass has reacted, fresh surfaces are not exposed and no more of the inert mass is rendered active. Therefore, for all practical purposes it can be left out of account altogether, and any attempt to assign to it a high molecular weight only confuses the issue.

For instance, a colloidal solution of metallic silver will react with Cl to give silver chloride, but the reaction is confined only to the surface molecules. Now we can either find its specific surface and consequently its active mass and consider the reaction as taking place in stoichiometric proportions, or we can give the silver particles a hypothetical high molecular weight and consider the entire colloidal solution in bulk. The main difficulty in accepting the first view has been that it has not so far been possible to determine the total surface of colloidal particles with even a reasonable amount of accuracy. This difficulty has at least been overcome in the case of soils, and the way has been cleared for a more rational view of the entire chemistry oi colloids. As a matter of fact colloid chemistry is the chemistry of surface molecules, not because they have acquired some mysterious property called adsorption, but because there is nothing extraordinary about the common or "garden" reactions between molecules. These molecules need not necessarily constitute the surface of particles of colloidal dimensions: they may be long strands, or plates, they may stay in suspension or may settle quickly. The major criterion – indeed the only criterion – is that its surface should be large enough to give an appreciable and measurable mass of molecules constituting the surface. As long as this condition is satisfied, as soon as this substance comes in contact with water, its surface will give a molecular solution and will take part in all the chemical reactions of which its molecules are capable – no more and no less.

It is convenient at this juncture to take some familiar examples of insoluble acids to prove the foregoing point. Stearic acid, for instance, is insoluble in water but dissolves in alcohol. We can, therefore, titrate an alcoholic solution; but when placed in water it

merely floats and does not combine with an alkali unless melted and thus reduced to the molecular state. It is completely insoluble in water, it has no surface, no active mass, and therefore does not combine with alkalies at ordinary temperature. If the acid is dissolved in alcohol and the alcoholic solution is dropped into a large excess of water in a thin stream while the liquid is violently agitated just underneath the nozzle, the precipitated stearic acid comes out in an extremely fine state of subdivision in which the size of particles is almost down to molecular dimensions. The precipitated acid is still insoluble in water. It does not form even a colloidal solution, but floats on the surface as a bulky mass which can be easily filtered, but retains a large amount of water in the interstices. It can be washed with water over a funnel without applying suction.

A portion of the wet acid titrated with $Ba(OH)_2$ solution gives a perfect titration curve with a well-defined inflection at the equivalent point, even though the acid is completely insoluble, as is its Ba salt (Figure 26).

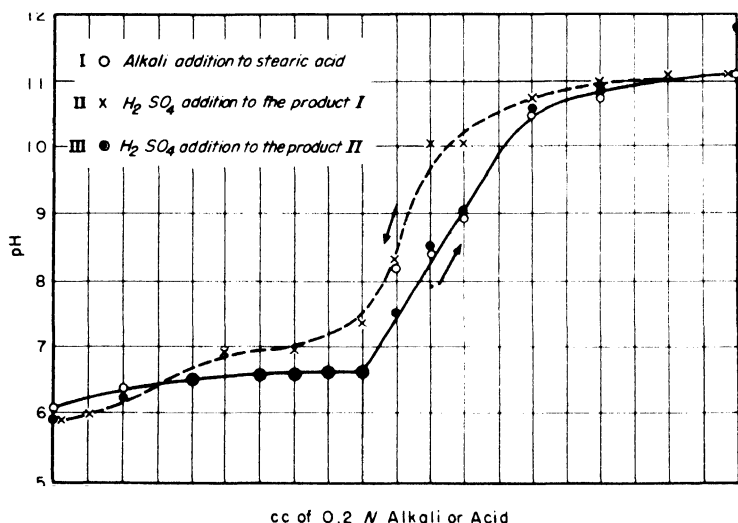



Fig. 26. Forward and Back Titration Curves of Stearic Acid with Barium Hydroxide and Sulfuric Acid

It can be titrated with $Ba(OH)_2$ solution using phenolphthalein indicator. Every time it is found to have 100% active mass. The barium stearate formed can be back-titrated with sulphuric acid and yields a perfect back-titration curve. The precipitated $BaSO_4$ can be separated quantitatively from the stearic acid which floats on the surface, whereas $BaSO_4$ settles out as a precipitate. The forward and backward titration of stearic acid with $Ba(OH)_2$ and H_2SO_4 can be repeated ad infinitum without affecting the course of the titration curve or changing the molecular state of the stearic

acid. This stearic acid in the wet state can be kept almost indefinitely without reduction in its active mass; it can still be titrated with alkali like any other soluble acid in the presence of a suitable indicator or electrometrically. But if it is allowed to dry, the active mass drops from 100% to only 10%, when the moisture is reduced from 98% to zero. Experiments with palmitic acid give almost identical results. The relation between active mass and moisture content in the case of these two acids is shown in Figure 27.

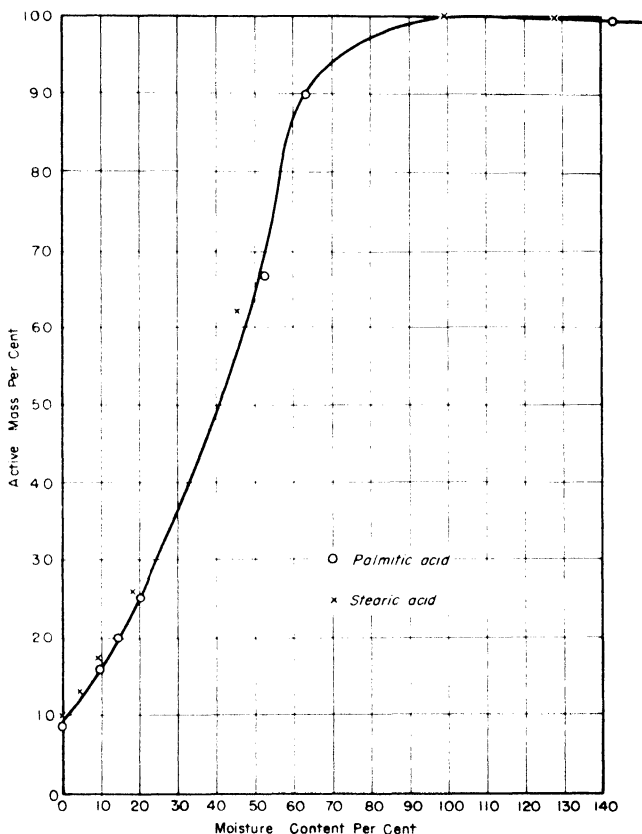



Fig. 27. Relation between Moisture Content and Active Mass of Stearic and Palmitic Acid

These results are extremely important in showing the part played by water in the development of intramolecular forces of cohesion. During the process of drying, as the water film recedes into minute capillaries and the radius of curvature becomes less and less, surface tension forces of greater and greater magnitude develop, with the result that the particles are drawn together by a negative pressure from the inside. It is remarkable that this negative pressure is of sufficient magnitude to draw the particles so close to one another that molecular forces of attraction come into play, and in-

tramolecular distances are so reduced that on subsequent wetting water molecules cannot get between them.

It might be mentioned, however, that the case of stearic and palmitic acids is rather different in the sense that these fatty acids are not entirely wetted by water. When they are first precipitated in the molecular state, the contact angle is zero, since naturally all the molecules are in contact with water. As the sample dries aggregates are formed, and even if the gaps thus created are much larger than molecular dimensions water may still not get into them. Thus even if the active mass is there, it cannot come into play unless the solid-air interface is replaced by solid-liquid interface.

A case in point is that of uric acid, which can be wetted by water. Though insoluble, it is so constituted that water molecules can enter the interstices, which are of sufficient magnitude to enable them to do so. This acid, even though completely insoluble in water, can be titrated with $Ba(OH)_2$, and gives a perfect titration curve in spite of the fact that Ba urate is also insoluble. When titrated in this manner the acid shows approximately 75% active mass, which rises to 100% when the acid and alkali are shaken together for 24 hours. Maximum amount of active mass is only obtained when excess alkali is shaken with the acid and the amount of alkali unreacted is filtered off and determined. It is likely that fresh surfaces are exposed on prolonged shaking with strong alkali, which otherwise may not have been accessible.

Silicic Acid and Alumina

We shall now consider the case of silicic acid which is particularly important in soils. An estimate of the active mass in freshly precipitated silica will throw considerable light on the nature of soil acidoids. Silicic acid is prepared by the addition of dilute HCl to sodium silicate, with rapid stirring. The gel is freed from salts by prolonged leaching with pure distilled water. During this process it is not allowed to dry. A portion of the wet sample is taken for titration while a similar portion is taken for moisture estimation by drying at 100 to 110°C. The wet sample is shaken with excess standard $Ba(OH)_2$ for varying lengths of time, at the end of which the unreacted portion of the $Ba(OH)_2$ is determined. The amount of $Ba(OH)_2$ taken up by a known weight of dry silicic acid gives the active mass of the sample. The results of this study are given in Table 15, and show that when moisture content stands at a level of several hundred per cent, drying the sample causes a reduction in its active mass.

It was found that there is no effect of ageing on silica gel as such. Freshly precipitated silicic acid was kept for a month with large excess of water without any effect on its active mass, which remained 100%. It is only when the moisture is reduced below a certain level that the effect of drying shows itself in a reduction in the active mass. It is interesting to note that the results are similar

to those obtained with stearic palmitic acid, and the phenomenon appears to be of universal application.

Alumina behaves exactly like silica in this respect. It is prepared by the addition of aluminum sulphate to a sodium hydroxide solution with rapid stirring, followed by filtration and leaching of the resulting alumina gel. Its estimation is also similar to that of silicic acid by reaction with excess of $Ba(OH)_2$. It is true that Ba aluminate has not been recognized as a possible salt of aluminic acid, but the fact of the matter is that this salt is actually formed in equivalent proportions with the active mass of aluminum hydroxide. Since it is insoluble it has escaped recognition, and only

Table 15. Relation between moisture content time of shaking and active mass of silicic acid.

Time shaking (days)	Active mass (per cent)					
	Moisture: 785%	589%	426%	150%	38%	13%
1	61.5	61.5	61.5	50.0	10.2	4.2
2	75.2	61.5	61.5	50.0	10.2	5.8
4	75.2	66.2	66.0	60.0	60.0	7.2
8	......	77.4	68.0	68.0	68.0	10.0
10	90.0	77.4	77.0	68.0	68.0	10.0
15	90.0	90.0	90.0	75.2	75.2	15.0

33.33 cc alkali used per gm. of silica is taken as 100% of active mass

Table 16. Relation between moisture content time of shaking and active mass of alumina gel.

Time of shaking (days)	Active mass (per cent)							
	Moisture:							
	3409%	2148%	733%	450%	266%	150%	50%	22%
1	100	90	61.0	60.0	45.0	30.0	15.3	4.8
2	100	90	70.0	70.2	45.0	30.0	18.0	10.2
4	100	90	85.8	72.2	50.0	30.0	23.6	15.4
8	100	90.5	86.3	72.2	62.2	45.0	......	......
10	100	100	91.6	83.3	72.0	45.0	29.8	19.3
15	100	100	91.9	92.0	72.0	46.6	30.7	23.5

36.0 cc alkali used per gm. of Al_2O_3 is taken as 100% active mass.

sodium aluminate has been studied. It might be pointed out that active mass due to surface solubility of a substance can be found only by reaction with a substance if the end product is insoluble; otherwise there is danger of fresh surfaces being exposed and the reaction proceeding to the end. Results with alumina gel similar to those with silicic acid are given in Table 16. Thirty-six cc of normal alkali used per gram of Al_2O_3 is taken as 100% active mass. Like silica gel there is no effect of ageing on alumina as long as the sample is kept at the maximum moisture content.

It is clear from the foregoing that the behavior of both silica and alumina, two of the most important constituents of soils, is capable of a very simple explanation based on well known laws of chemical equivalence. It is significant that even with freshly precipitated gels, the theoretical amount (corresponding to 100% active mass) is never exceeded. The time of shaking or the concentration of $Ba(OH)_2$ has some effect when the active mass is less than 100 due to aggregation. It is understood that the cohesive forces coming into play during the drying process will depend on the size of the capillaries and the chance association of the particles. These cohesive forces would naturally vary at different stages of drying, and surfaces that are not exposed might become so on shaking for varying lengths of time; or the actual physical penetration of the reacting solution in the minutest capillaries may be a slow process, as it is bound to be since this can take place only by diffusion of solvent from one place to another, through capillaries of molecular dimensions.

It is, therefore, characteristic of all silicates and soils that their reaction with alkalies proceeds very slowly after the initial neutralization, which is very rapid. However, it is not necessary to call that portion of the acidoid which reacts slowly by any other name, for fundamentally it is in no way different from the portion that reacts instantaneously. The difference is purely due to the difficulty of mechanical accessibility of the acidoid to the alkali.

In a freshly precipitated silicic acid, when the active mass is 100% and the particles have not formed aggregates, the reaction with alkalies is instantaneous, as if the entire mass were in molecular solution. The speed of reaction when silica, alumina or aluminum silicate has been dried must depend on the strength of the alkali. This is an inherent error in the determination of the titration curves of such substances. The titration curve must undergo a twist, for all parts may not refer to the same active mass. At higher concentrations of alkali some extra surfaces may be exposed which were not operative at lower concentrations. Indeed it is not certain that the entire mass may not react, provided the strength of the alkali is high enough and the time of shaking very long. It has been shown that a state of equilibrium in the case of soils is not reached even in three months.

Thus we may be tempted to distinguish between the active mass that is in surface solution and the active mass that can be brought into solution on prolonged shaking. Such a distinction, however, could equally well be made between the portion of any substance actually in solution and the portion remaining in the solid state which could be brought into solution by prolonged shaking. It is the slow accessibility of the micro-capillaries to the reacting fluid which is the cause of slow rate of reaction. Or perhaps we might put it this way: it is the slow rate of diffusion of the alkali through the liquid in the minute capillaries between the aggregates that

causes this time lag. For this reason, when the soil is completely dispersed by first converting it into a sodium saloid and then treating with HCl to convert it into the acidoid, the rate of reaction with alkalies is rendered almost instantaneous. It will be recalled that this technique is recommended when studying the heat of neutralization of soil acidoids.

It is also to be remembered that in soils a portion of the aluminosilicate actually may go into true solution by the formation of aluminates if a strong alkali like NaOH is used. When this happens fresh surfaces will be exposed and more of the alkali may react.

CHAPTER X

EFFECT OF IGNITION ON SOIL ACIDOIDS

Heating soils to a high temperature is known to destroy their colloidal properties. The exact temperature at which this may take place has been shown to vary from 300 to 700°C, depending on the silica sesquioxide ratio. If we regard the soil as hydrated ferroaluminosilicate, we can well imagine the change in its properties likely to be brought about by heating. It seems fairly certain that most of the outstanding colloidal properties of soil must be associated with the presence of water of hydration, and the primary effect of heating must lie in the removal of this water.

A number of physical properties like plasticity and cohesion, which may be due to the water of hydration, are likely to be destroyed completely when this water is driven out. It is of interest to know how far the acidoid properties of the soil are affected by progressive heating, and what is the nature of the change that takes place in the ferroaluminosilicates.

In order to avoid complications, the soils used for this study, unless otherwise stated, were acid-treated and converted into acidoid. The following properties were studied before and after heating them to various temperatures: titration curves, base equivalent, reaction with ammonia, production of free alkali, destruction of humus and decomposition of calcium carbonate, and loss of weight on ignition (dehydration). A black cotton soil containing 56% of clay was used for this study in the first instance. After converting it into the acidoid it was heated to different temperatures for 6 hours in an electric muffle furnace. Titration curves with NaOH were determined with the glass electrode and T/2 and pK values were found from the titration curves, as explained previously. The titration curves are shown in Figure 28 and the pK values are given in Table 17.

It will be seen that the T/2 value is hardly affected by ignition, though the values show rather large variations because of the difficulty of interpolation in the flat portion of the titration curves. The titration curves as well as the pH values show a considerable change on heating. Ignition seems to have the effect of making the soil acidoid weaker, its total quantity virtually remaining the same. Base equivalent was also determined by first converting into K

saloid and then displacing the K by treatment with ammonium carbonate, as well as by ammonia reaction (in the cold). These values are included in Table 17. Base equivalent as determined by these methods is not affected appreciably up to 400°C. Ignition above this temperature leads to a progressive decrease, which is consistent with other changes that seem to take place when the soil is heated at a higher temperature.

Table 17. Effect of ignition on soil acidoid

Temperature (°C)	pK	Base equivalent (m.e./100 gms. of soil		
		T/2	NH_3 reaction	KCl leaching after KOH treatment
95	5.07	48.0	64.4	47.9
225	5.36	39.0	64.1	48.1
300	5.62	45.2	59.9	48.4
400	6.11	41.4	52.1	49.1
520	6.20	35.2	51.0	44.6
610	6.98	41.7	49.7	41.8
700	7.54	50.0	33.8	33.9
800	7.84	39.1		
910	8.69	52.0		

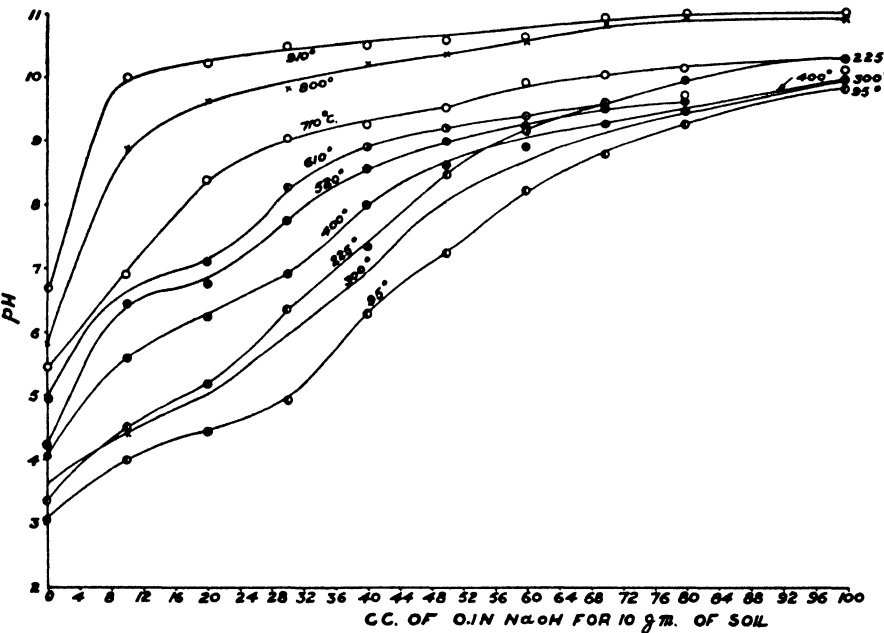



Fig. 28. Titration Curves of P.C. 13 A.T. Soil Heated to Various Temperatures

Production of Free Alkali

We have seen that the acidoid properties of soil are partly destroyed on heating. It appeared logical to conclude from this that, if the soil acidoid were neutralized with a base and heated, part or all of the base might be released. This supposition appeared to

offer attractive possibilities of determining the bases neutralizing a soil free from $CaCO_3$ by igniting it. Sodium saloid obtained by neutralizing a H soil to various pH values was ignited and the amount of alkali set free was determined. It was found that hardly any alkali which could be leached out was liberated as long as the quantity did not exceed the T/2 value.

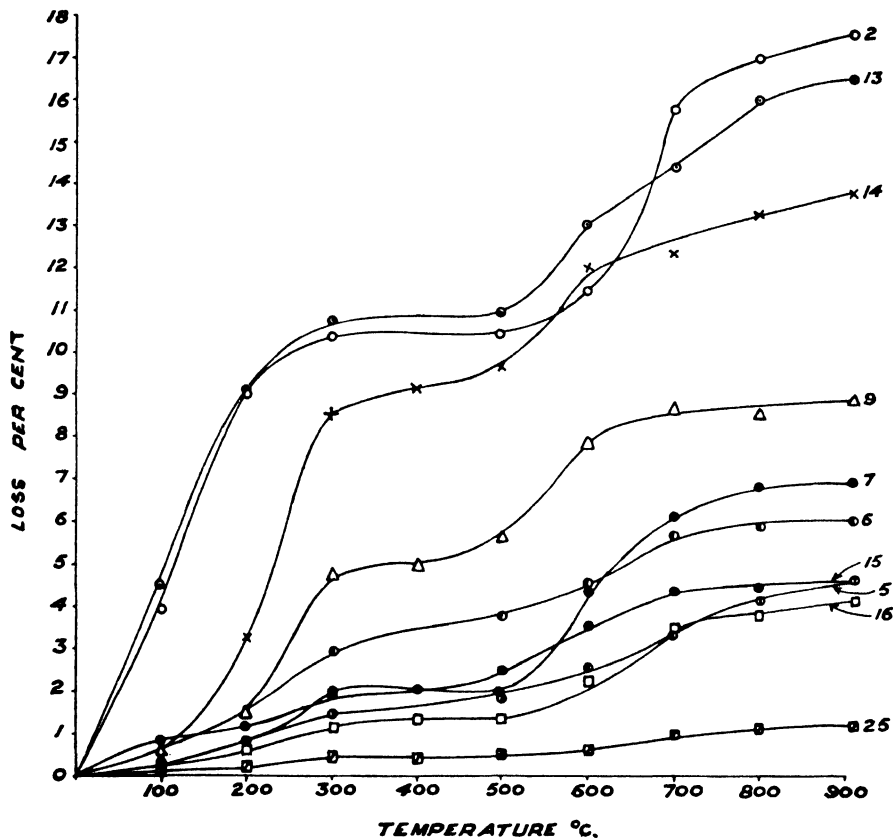



Fig. 29. Loss of Weight on Ignition of Natural Soils

This result is very important, as it appears to give us an insight into the real mechanism of the destruction of the colloidal properties of soil on ignition. If ignition merely resulted in dehydration and destruction of the acidoid property, then alkali would necessarily be set free. If, on the other hand, ignition caused a fusion of the smaller particles into larger aggregates, than no alkali would be liberated. The latter view is confirmed by the fact that if a soil containing sodium or calcium saloid is ignited, all of the base becomes fixed in the non-replaceable form and cannot be replaced when shaken with a neutral salt. The progressive increase in the pH value of a H soil on heating also leads to the same conclusion. It must be understood that a soil, on drying, can form water-stable

aggregates, but these aggregates can always be resolved into individual particles by mechanical or chemical methods of dispersion. Ignition, on the other hand, causes the formation of permanent aggregates that cannot be resolved by physicochemical treatments into the smaller particles originally present. These aggregates are in all respects similar to larger particles and correspond in properties to silt fractions in natural soils.

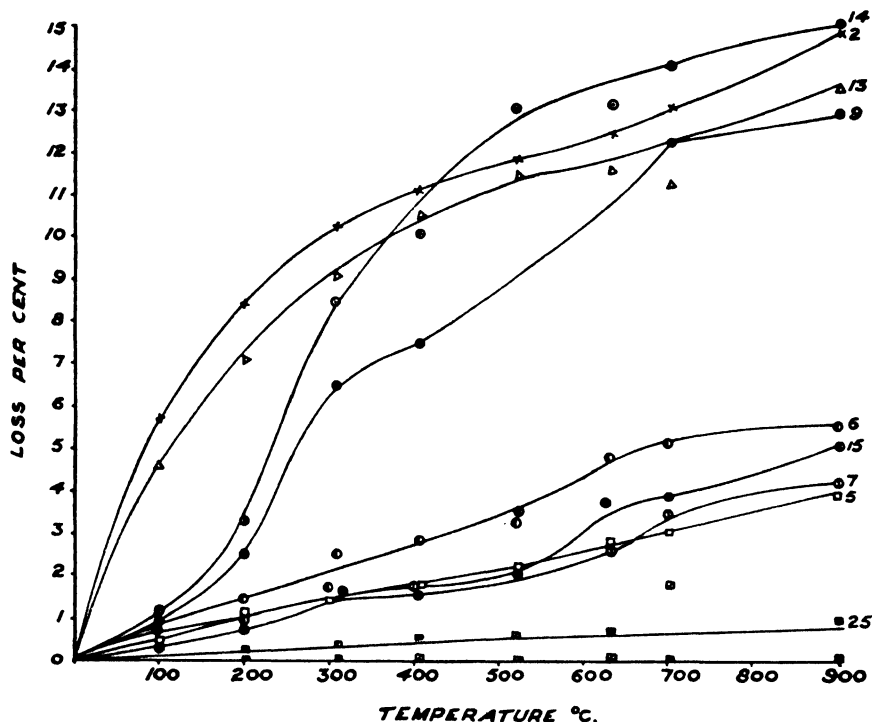



Fig. 30. Loss of Weight on Ignition of Acid-Treated Soils

Destruction of Humus and Decomposition of $CaCO_3$

Destruction of humus and the decomposition of $CaCO_3$ are two of the most important changes intimately associated with the ignition of soils, though not directly concerned with its colloidal properties. The total loss of weight accompanying the ignition of soils is made up of the following factors: dehydration, destruction of the organic matter or humus, and decomposition of $CaCO_3$.

In order to determine the magnitude of each factor, a number of soils were heated to different temperatures in the natural state, after acid treatment (destruction of $CaCO_3$), and after treatment with alkaline permanganate (destruction of humus). The progressive loss of weight against the temperature of heating is shown in Figures 29, 30 and 31, respectively.

The curves for various soils show a remarkable similarity. The curve for the decomposition of calcium carbonate alone is also shown in Figure 31. Humus is completely consumed at 400°C. The

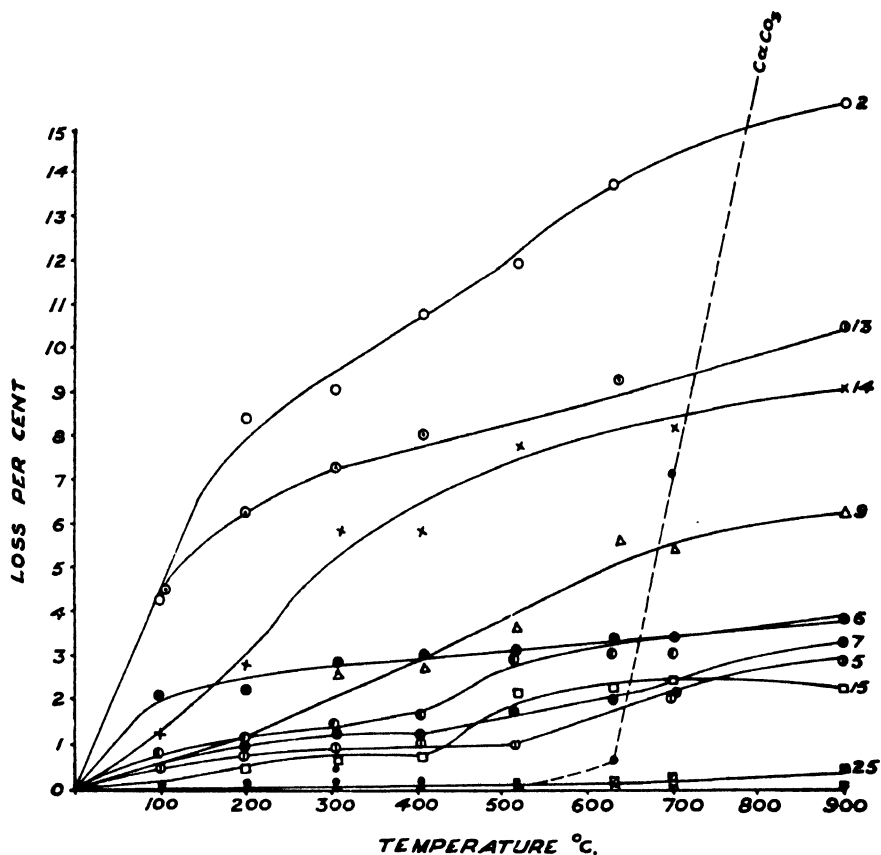



Fig. 31. Loss of Weight on Ignition of Humus-Free Soils

major portion of the loss in weight on heating is confined to temperatures below 500°C. Calcium carbonate, on the other hand, is hardly decomposed at this temperature and at 600°C its decomposition is practically complete.

CHAPTER XI

ACID SOILS IN NATURE

A discussion of the properties and chemical reactions of soil acidoids cannot be closed without reference to acid or "sour" soils. These soils have been known to farmers from time immemorial. Intelligent farmers even discovered the use of lime to counteract soil sourness long before they knew anything of the reaction involved. The soil scientists who followed in their wake fared no better. A number of empirical methods of finding lime requirements of soil came into existence, which have been briefly touched upon in an earlier chapter. Since the addition of excess limestone had no adverse effect, and since even the smallest amount added to a sour soil had a beneficial effect, the efficacy or otherwise of the method was never found out and rarely questioned.

The following fundamental facts emerge from a study of the formation and chemical reactions of soil acidoids, which have a bearing on sour soils.

(1) Saloids of soil acidoids are weak and easily hydrolyzed in water – much more easily up to the limit of the first hydrogen. In nature this hydrolysis is aided by the CO_2 in rain water, which can bring about the complete transformation of the saloids into acidoids. Soil acidoids therefore are characteristic of humid regions where rainfall is heavy.

(2) Plants cannot thrive in acidoids, which must be neutralized with bases and converted into saloids. The limit of this neutralization must be the first hydrogen of the dibasic acidoid. This will correspond approximately to a pH value of 7 when it is a Ca saloid, a little less with Mg saloid, and as much as 8.5 to 9 with Na saloid. The pH value of a natural soil represents a single point on its titration curve as a result of the dynamic equilibrium between natural agencies which bring about the removal of bases as well as their restoration.

(3) When the depletion of the bases or the conversion of the saloid into the acidoid has gone beyond a certain limit, the plants begin to suffer until a stage is reached at which the formation of the acidoid is nearly complete, when it is unable to support any vegetation. Within this range of partial depletion some plants can thrive better

than others. Therefore as the soil is gradually depleted, botanical flora undergo profound changes, until all plants except those specially adapted to thrive in an acid medium are eliminated.

(4) A barren acidoid soil, when gradually revived by the addition of lime, undergoes a similar change in the reverse direction, and therefore the limit to which it should be neutralized must depend on the type of crop intended to be grown on it. For most crops the

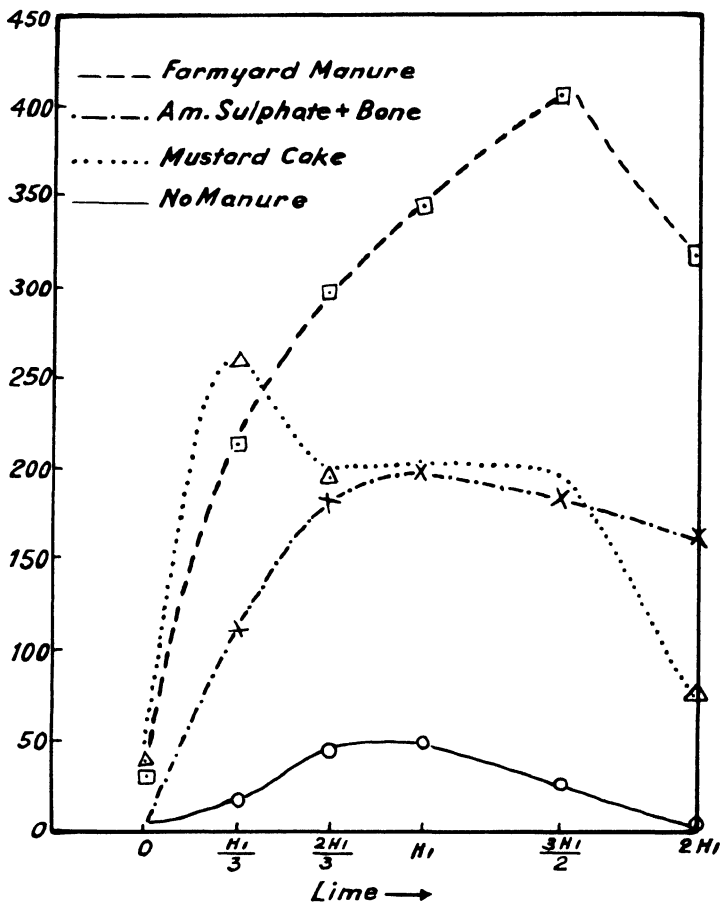



Fig. 32. Yield of Green Fodder with Increasing Doses of Lime

point of neutrality, i.e., pH 7, is the best. This limit need never be exceeded, though in some cases a smaller quantity of lime and the attainment of a lower pH value will be good enough.

(5) Not only will the optimum dose of lime depend on the nature of the crop, but also the type of additional manure to be used with liming. This is well illustrated by the results of an actual field experiment conducted by the author in which an acid soil was gradually neutralized with lime to the extent of normal saloid formation. From the results of crop yield plotted in Figure 32 it is quite clear

that lime requirement is not exceeded beyond the neutralization of the first hydrogen; but what is more remarkable is the fact that in the presence of ammonium sulphate and bone or mustard cake the quantity of lime required is much less than even the base equivalent up to the neutralization of the first hydrogen. Another point worthy of note is that there is a distinct fall in crop yield when the amount of lime added exceeds a certain limit. This is an important point which is well worth further study.

It would appear from the foregoing discussion that the lime requirement of a soil is not a fundamental single value constant like its base equivalent, but must vary with the nature of the crop and of the manure. In the absence of other manures lime alone is quite inadequate to give anything except a bare apology for some vegetative growth, and the presence of other substances has a profound influence in modifying or accentuating the influence of lime.

It must be remembered that soil acidoid and its various saloids would be classed as weak electrolytes, feebly ionized. The relative influence on these saloids of strong electrolytes present in artificial manures must be great. All the trace elements, for instance, which are so important for healthy normal growth of plants and the lack of which sometimes proves disastrous, are likely to be affected profoundly by the presence of inorganic salts in artificial manure. This may be one of the reasons why fields supplied with artificial manures year after year sometimes give lower and lower crop yields. So far no attempt has been made to study the changes that might be brought about in the equilibrium between soil acidoid-saloids by the introduction of inorganic salts commonly present in manures, except in the light of the imperfectly understood base exchange. Once the principles involved in these reactions have been grasped we shall have no difficulty in predicting what is likely to happen chemically when a manure is added to the soil, irrespective of what nutrients it is likely to supply to the plant.

With our imperfect knowledge of the chemistry of the soil, the tendency has been to ignore the soil altogether and rely more and more on quick tests, on estimates or on experience to decide what manure should be added. It has been supposed that a manure can do no harm, and that if too little is added, the improvement in crop yield may not be very great, but it will still be appreciable. Thus there is a wide latitude in which to play about with field methods and quick tests. But this is hardly a scientific method of approach.

From a study of the influence of exchangeable ions in soil colloids on bacterial activity and plant growth, the author in collaboration with Joshi* learned the following facts:

(1) Cultures of bacteria on plants did not thrive when introduced in soil acidoid.

(2) When the first hydrogen of the dibasic acidoid was neutralized with a base, bacteria as well as plants could survive in it.

*_Mem. Dept. Agr. Ind._, Vol. 11, No. 4 (1930).

(3) Nitrification, nitrogen fixation, and plant growth are inhibited in the presence of free acidoid. Ammonification, however, appears to proceed normally in such soils.

(4) There is no evidence that sodium saloid, which is the main constituent of alkali soils, is directly toxic to plants. The toxicity of these saloids is mainly due to the adverse physical conditions set up by this saloid.

CHAPTER XII

CALCIUM SALOIDS

Calcium saloids form by far the largest proportion of agricultural lands all over the world. Calcium is so important from the point of view of crop growth that all good agricultural soils may be said to consist of calcium saloids. A calcium saloid can be formed (a) by the action of lime on soil acidoid; (b) by the action of $CaCO_3$ on soil acidoid; (c) by exhaustive leaching of acidoid or any other saloid with a soluble calcium salt. In the first method the acidoid can be completely neutralized; in the second, mono-acid saloid will be formed in the cold and the normal saloid on heating; in the third, the amount of saloid formed will depend on the nature of the calcium salt used for leaching and the extent of neutralization of the acidoid. This point will be dealt with in greater detail later.

Soils containing calcium saloids generally have a good tilth and are sufficiently porous to allow the free passage of water and air. Aeration for plant roots is as important as breathing for human beings and animals. Unless grown in porous soils, in which free circulation of air can take place, plants would die of suffocation. Rice and certain other aquatic plants can somehow make use of the air dissolved in the irrigation water; but for ordinary agricultural crops root aeration is absolutely necessary. Clods of soils containing calcium saloid are easily broken when slightly moist, and less energy is expended in ploughing and opening up such soils. These soils generally remain in good tilth. It is difficult to define good tilth, but the farmer knows quite well what is meant by it. It is due to a combination of factors, not the least important of which is the nature of the saloid it contains.

A Ca saloid when shaken with water settles quickly; if water is poured on it, it is absorbed quickly and the soil lump disintegrates (but does not disperse). Water channels made in a soil containing Ca saloids cause much loss of water due to seepage. $CaCO_3$ sometimes accumulates in soils to the extent of as much as 30 to 40% giving them a calcareous character. Such soils, of course, always contain the maximum amount of Ca saloid, and always maintain an excellent tilth. The cultivation of such soils is the easiest, as they offer the least resistance to the movement of the plow. The formation of calcareous soils is largely due to the shells of snails and

other small animals that can accumulate calcium carbonate around their bodies; such soils are generally alluvial, i.e., they have been transported and deposited by water.

Estimation of Calcium in a Calcium Saloid

Estimation of Ca in a saloid is exactly like its estimation in a soluble Ca salt. Any one of the following methods can be used.

Na_2CO_3 method.* When Na_2CO_3 is added to Ca-H saloid, all the Ca is precipitated as carbonate and an equivalent amount of Na saloid is formed. At the same time the Ca-H saloid is further neutralized with the formation of normal Na saloid, and an equivalent amount of CO_2 is set free, which immediately combines with the $NaCO_3$ to give bicarbonate. In the end we are left with a mixture of sodium carbonate and bicarbonate. These can be estimated in the presence of each other. The decrease in the concentration of CO_2 in the original solution is taken as equivalent to the Ca in the Ca saloid. The bicarbonate found is of course equivalent to the acidoid. Thus in extreme cases if no Ca saloid is present there will be no decrease in the concentration of total CO_2 in the carbonate, and if no acidoid is present, there will be no bicarbonate formed. Obviously the method is applicable in the presence of excess of $CaCO_3$. Humus, on the other hand, interferes in this estimation, as the carbonate solution on shaking is dark colored and cannot be titrated in the presence of indicators. However, if the reaction is carried out at 0^oC no humus comes in solution.

Potassium oxalate-acetate-carbonate method.* This method is based on the principle that the Ca in a Ca saloid is quantitatively precipitated as oxalate on the addition of K oxalate. The use of K acetate facilitates the formulation of granular Ca oxalate and renders the precipitation rapid. K carbonate is used to make the $CaCO_3$ in the soil completely insoluble, so that it is not reacted by the oxalate. In place of K oxalate, acetate and carbonate, ammonium oxalate, acetate and carbonate can be used. This has the advantage that Na, K and Mg saloids, if present, are brought into solution and can be estimated by evaporating and igniting the ammonium salts.

The application of the above well known analytical methods to the estimation of Ca in Ca saloids leads one to the irresistible conclusion that the so-called exchangeable Ca in soils exists in chemical combination with the alumino-silicates, and that all exchangeable bases must be regarded as saloids possessing all the properties of weak electrolytes. As opposed to the above simple treatment methods, a number of methods for estimating exchangeable Ca have been suggested. These rely on the principle that the Ca saloid can be converted into any other saloid by exhaustively leaching it with a neutral or hydrolyzed salt. The displaced Ca is estimated in the leachate by the usual analytical methods.

In order to show that the estimation of Ca in calcium saloid is capable of being raised to the status of an exact analytical method

*Both methods are described in detail in *Soil Sci.*, 42:47 (1936).

which can be carried out in a variety of ways, a number of soils were examined by the following methods:

(a) NaCl method: Ten grams of soil is leached with 1000 cc of 0.2N NaCl in 100-cc lots, followed by another 1000 cc leaching in the same way. Ca is determined in the two leachates separately, and the difference between the two is taken as equivalent to Ca in the saloid.

(b) KCl method: Exactly like (a), but 0.2N KCl is used instead of NaCl.

(c) Ammonium acetate method: Ten grams of soil is leached with one liter of N ammonium acetate in 100-cc lots; Ca is determined in an aliquot of the leachate. This method is used for carbonate-free soils only.

(d) NH_4Cl method: Ten grams of soil is leached with 1 liter of normal NH_4Cl in 100-cc lots; Ca is determined in the leachate. This method is used for carbonate-free soils only.

(e) $(NH_4)_2CO_3$ method: Ten grams of soil is leached with 500 cc of normal $(NH_4)_2CO_3$. Total ammonia taken up by the soil minus the exchangeable Na, K and Mg in the leachate is taken as equivalent to Ca in the Ca saloid.

(f) Na_2CO_3-NaCl method: Ten grams of soil is shaken for two hours with 200 cc of 0.1N Na_2CO_3 solution in N NaCl. An aliquot of the filtrate is titrated with standard acid, using first phenolphthalein and then methyl orange as indicator. The decrease in the concentration of CO_2 ion is taken as equivalent to exchangeable Ca.

(g) K_2CO_3-KCl method: Exactly like (f), but K salts are used instead of Na salts.

(h) K oxalate-acetate-carbonate method: Ten grams of soil is shaken occasionally by the hand in a stoppered bottle with 100 cc of a solution N with respect to K acetate, 0.1N with respect to K oxalate, and 0.015N with respect to K_2CO_3, filtered, and 50 cc of the filtrate titrated with 0.1N $KMnO_4$. The total decrease in the concentration of oxalate ion is equivalent to Ca in the Ca saloid. If the room temperature is high, the suspension should be cooled to $10^{\circ}C$.

(i) K oxalate-chloride-carbonate method: Exactly like (h) except that KCl is used in place of K acetate.

(j) Ammonium oxalate-acetate-carbonate method: Exactly as in method (h) except that the solution used is 0.1N with respect to ammonium oxalate, 0.5N with respect to ammonium acetate, and 0.25N with respect to ammonium carbonate.

(k) Ammonium oxalate-acetate method: Exactly like (j) but without $(NH_4)_2CO_3$. This method is used for carbonate-free soils only.

The results of this comparison are given in Tables 18 and 19. The various methods show a good agreement considering the inaccuracy of leaching methods.

The methods discussed in the foregoing obviously are not applica-

ble to soils containing gypsum, which must be removed or rendered insoluble before they can be applied. A technique was developed by which all the $CaSO_4$ is converted into $CaCO_3$. Briefly, this method consists in shaking the soil suspension with excess of $BaCO_3$, when the reaction $CaSO_4 + BaCO_3 \longrightarrow CaCO_3 + BaSO_4$ takes place. The excess $BaCO_3$ as well as the products of reaction are all insoluble

Table 18. Ca Saloid in Calcareous soils by various methods

Soil No.	$CaCO_3$ per cent	Clay per cent	Ca saloid per 100 gm. soil								Na + K	Mg.	pH
			(A)	(B)	(E)	(F)	(G)	(H)	(I)	(J)			
			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	
1	36.0	11.3	5.4	5.1	3.9	5.3	4.8	7.6	4.1	8.4	0.4	1.7	8.41
2	4.9	59.3	47.9	47.9	49.9	52.3	55.7	49.6	46.2	48.0	2.3	10.0	8.21
4	0.8	15.2	9.1	6.2	7.0	5.4	8.4	9.0	7.4	8.4	0.4	0.6	8.55
5	1.6	12.3	7.0	6.0	6.1	5.3	8.4	9.1	6.6	8.6	0.2	1.0	8.77
7	5.6	21.8	3.0	0	1.4	1.9	3.4	3.9	2.2	2.0	9.2	5.8	9.58
8	0.6	25.2	18.3	16.7	16.9	18.3	19.8	21.2	19.0	19.0	1.0	2.0	8.41
10	1.0	35.6	20.7	19.2	19.2	23.5	23.2	25.5	22.8	22.0	1.5	3.3	8.71
11	2.3	32.8	23.1	22.2	21.4	25.9	27.6	28.1	26.0	28.4	0.8	4.6	8.77
13	1.8	58.9	48.3	49.2	53.8	55.3	54.8	55.6	50.6	51.0	0.4	5.5	8.53
16	2.2	7.3	3.6	3.5	4.1	2.9	3.6	5.8	4.4	5.8	0.2	2.9	8.74
17	0.7	14.2	9.0	7.6	7.8	7.8	10.4	8.6	7.2	......	......	......	8.20
19	1.2	42.4	15.4	16.8	19.5	18.1	21.0	19.0	17.2	18.0	0.5	3.0	8.40
21	3.3	13.5	7.0	8.8	10.4	6.1	11.4	12.0	9.0	......	......	......	8.25

Table 19. Calcium saloid in carbonate-free soils by various methods.

Soil No.	pH	Clay per cent	Ca saloid per 100 gm. soil							Na + K	Mg.
			(C)	(D)	(F)	(H)	(I)	(J)	(K)		
			m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
-3 .	7.64	62.3	53.8	50.8	53.2	55.8	53.4	51.4	59.6	1.1	12.4
6	5.29	28.4	5.1	4.9	0.6	6.3	3.8	4.2	5.4	0.3	1.5
9	5.76	21.6	3.8	4.4	0.6	4.2	1.3	2.2	4.6	0.9	0.8
12	5.84	3.8	3.6	3.9	0	4.4	0	2.2	3.2	0.7	1.6
14	5.37	22.3	2.8	3.7	5.7	5.6	6.0	5.4	5.0	0.1	0.6
15	7.71	21.9	13.0	13.9	12.0	12.0	8.6	8.6	12.0	0.1	0.9
18	5.79	22.2	4.1	4.3	4.5	4.0	2.2	......	.3.6	......	......
20	5.64	6.5	3.1	4.8	4.5	2.3	......	0.2	2.2	0.1	1.2
22	6.85	15.2	7.8	8.1	8.2	8.5	......	......	8.5	......	......
23	7.41	11.3	8.2	9.0	5.6	8.4	6.5	......	9.0	......	......

in the medium in which the final precipitation of the Ca in the saloid is effected, and therefore do not affect the results.

If the soil contains sulphates of alkali metals besides $CaSO_4$, these must be removed by leaching with alcohol (rectified spirit), before the soil is shaken with $BaCO_3$. The reason for this precaution is that alkali sulphates can react with $BaCO_3$ to give $BaSO_4$ and alkali carbonates, and the latter can react with Ca saloid and precipitate Ca as $CaCO_3$; therefore, at the end of the first reaction, some of the Ca in the Ca saloid will be removed along with $CaSO_4$. Leaching with alcohol leaves the soil in a friable state on drying,

and it can be detached easily from the filter paper for the determination of Ca in the saloid.

As an example of the practical application of these methods the analyses are recorded of certain soils from Sind (Pakistan) which contain $CaCl_2$, $CaSO_4$, Na_2SO_4 and NaCl (Table 20). Incidentally the technique developed herein enables us to differentiate between the various forms of Ca. The following determinations were made: (a) The soil was leached with 200 cc of alcohol and the filtrate examined for $CaCl_2$ and alkali salts. (b) The alcohol-leached soil was shaken with 50 cc of water and 1 gm of $BaCO_3$ and then examined for Ca in the saloid. (c) The alcohol-leached soil was examined for Ca saloid without being shaken with $BaCO_3$. (a) gave $CaCl_2$, (c-b) gave $CaSO_4$; and (b) gave Ca in Ca saloid.

Table 20. Various forms of Ca in Sind soils

Soil No.	Soluble salts (%)	Ca in various forms (m.e./100 gm. soil)		
		Ca Saloid	$CaSO_4$	$CaCl_2$
1	18.2	3.2	5.2	28.4
3	15.8	5.2	2.4	29.8
4	29.2	4.6	30.6	19.6
7	23.0	4.6	23.6	25.8
8	10.7	0	15.6	3.6
9	2.2	7.0	9.4	7.0
10	57.4	2.2	32.0	7.0
12	13.3	6.4	2.8	30.0

These results bring out clearly the characteristic differences in the soils. It will be seen that a number of soils, although containing a large amount of water-soluble Ca, have very little Ca saloid. This is, of course, due to a very large excess of Na salts.

The fact that $NaCO_3$ can lead to the complete precipitation of Ca in the Ca saloid throws an interesting sidelight on the cause of barrenness in alkali soils. It is not improbable that plants are unable to grow in such soils on account of Ca deficiency, no doubt brought about by the $NaCO_3$ which is invariably present in them.

CHAPTER XIII

SODIUM SALOIDS

Rainfall has a profound influence on soils. A high rainfall leads to the formation of soil acidoids, and in regions of medium rainfall Ca saloids are the general rule. The third important group of soils, namely those containing Na saloids, are found in arid or semi-arid regions. There are thousands of acres of such soils scattered all over the tropical countries.

Sodium saloid of the soil can be easily prepared by neutralizing the acidoid with NaOH or Na_2CO_3. The latter can also be used for converting a Ca saloid into a Na saloid. It can also be prepared by leaching any saloid with a solution of a Na salt. That is how most of the Na saloids in nature are supposed to have been formed, namely, by the action of sea water rich in Na salts.

Soils containing Na saloids are highly alkaline, i.e., their pH value is high and may go up to 10.5. These soils when shaken with water remain in suspension for days; and when water is poured over them it may stay there without being absorbed. When dry, Na saloids are hard, like stone, and no plough can break them. Even blasting with dynamite has been tried to break them open, but with only indifferent success.

Soils containing Na saloids are naturally barren, for water cannot move into them, air cannot pass through them, roots cannot penetrate them, and therefore no plant can grow in them. In tropical countries (such as Western Pakistan) there are miles and miles of such lands, without a blade of grass on them, where one could comfortably drive a car at 50 miles per hour. If one were riding a horse, the hoofs would give a metallic ring as if on a stone pavement.

The presence of Na saloid in a soil has a profound influence on crop growth, and for all such soils it is a matter of considerable importance to know how much sodium saloid they contain. This can be done by one of the following methods:

(a) Shake the soil with Ca or Ba hydroxide solution. When the Na saloid is converted into Ca saloid, the displaced Na appears as hydroxide. An aliquot of the filtrate when treated with ammonium carbonate precipitates Ca or Ba, leaving Na_2CO_3 in solution, which is equivalent to the Na in the sodium saloid and is easily determined in the filtrate.

(b) Shake the soil with ammonium carbonate solution; when ammonium saloid is produced all the displaced Na appears as Na_2CO_3 in solution, which is evaporated to dryness and the residue of Na_2CO_3, which is equivalent to the Na in the saloid, is determined by titration with standard acid.

If the soil contains humus, method (a) is more suitable; in all other cases method (b) is more convenient. Both give the same results, so it is not necessary to specify the method when recording the results. Ammonium carbonate method is applicable in the case of soils even in the presence of soluble Na salts. The $Ba(OH)_2$ method is not applicable when the soil contains sodium sulphate.

Of course Na saloid can be determined by leaching with a neutral salt and estimating Na in the leachate, but the analytical difficulties of estimating Na, as well as the error due to the presence of Na salts, make this procedure extremely tedious.

Degree of Alkalization

With the help of the simple methods of estimating Na saloid, which is the main cause of infertility in alkaline soils, we can determine the influence of this saloid on crop yield in areas characterized by such soils. For this purpose it is convenient to make use of the ratio called the degree of alkalization (D.A.), which may be defined as the ratio of the amount of Na and K saloids present in the soil (n) to the maximum amount of monovalent saloids the soil is capable of forming by exhaustive treatment with a neutral salt of Na or K (N), or:

$$\text{D. A.} = \frac{100n}{N}$$

A word about the inclusion of K in the degree of alkalization. This is purely a matter of convenience. The properties of K saloid are not similar to those of Na saloid, but the amount of K saloid in an alkali soil is generally so small that its separate estimation would make the method unnecessarily tedious without any corresponding advantage. It is also more convenient to use a K salt for leaching with a neutral salt. This makes no difference in the results, but if humus is present the leachate with NaCl is dark-colored and leaching is slow and difficult. The outline of the method of estimating D. A. is as follows:

Ten grams of the soil is shaken with 100 cc of 0.2N $(NH_4)_2CO_3$ for about two hours. Occasional shaking by hand is all that is necessary. It is then filtered through a Buchner funnel with the filter paper stuck to it with wax and leached with another 100 cc of the same solution. The filtrate is evaporated to dryness and the residue of Na and K carbonate, equivalent to the Na and K saloids in the soil, is determined by titration. This gives us the value of n. The soil on the Buchner funnel is then leached with 200 cc of 0.2N KCl solution in 50 cc lots. The leachate is discarded. The soil is again

leached with 200 cc of 0.2N $(NH_4)_2CO_3$ in 50 cc lots and the displaced K_2CO_3 determined in the leachate exactly as before by evaporating it to dryness. This gives us the value of N. From the values of (n) and (N), the D. A. is calculated.

A number of alkaline-soil samples from fields on which reclamation experiments were being carried out were examined according to the method described in the foregoing. The object was to ascertain whether cultural treatment and crop yields were reflected in the (D. A.) values for the various soils. The number of soil samples examined is small, but is sufficient to illustrate the profound influence of this factor on crop yield.

The results given in Table 21 indicate the usefulness of the (D. A.) values in characterizing alkali soils.

Table 21. Degree of alkalization & yield of wheat grain in Kala Shah Kaku soils

Soil No.	Treatment	n (m.e. %)	N (m.e. %)	D.A. (%)	yield (lbs. per acre)
1	Control	7.74	10.51	73.6	123
2	$CaCl_2$ @ 2 tons p.a.	2.92	10.10	28.9	693
3	Control	8.17	10.66	76.6	406
4	$CaSO_4$ 2 tons p.a.	6.03	10.46	57.6	496
5	Control	7.90	10.36	76.6	166
6	Control	8.00	9.80	81.6	214
7	$CaCl_2$ @ 1.5 tons p.a.	3.40	8.14	41.8	867
8	Control	5.00	9.05	55.2	818
9	$CaSO_4$ @ 1.5 tons p.a.	3.24	8.78	36.9	798
10	Control	4.00	8.00	50.0	687
11	Flooding & washing	1.37	8.37	16.4	1,036
12	Control	2.80	8.67	32.3	770
13	$CaCl_2$ @ 1 ton p.a.	2.30	8.47	27.2	737
14	Control	2.72	8.62	31.6	828
15	$CaSO_4$ @ 1 ton p.a.	3.23	8.88	36.4	867
16	Control	3.23	8.57	37.7	1,019
17	Flooding & washing	3.10	8.16	38.0	1,081

In almost all cases the reclamation of an alkali soil has brought about a marked reduction in the degree of alkalization. There is also a significant correlation between crop yield and (D. A.) value of different soils, as illustrated in Figure 33. The actual correlation coefficient between the two sets of values worked out to be -0.85 for both Kala Shah Kaku and Montgomery soils when treated separately, and -0.76 for the whole series. It will be seen that in Kala Shah Kaku soils a higher degree of alkalization has been tolerated than in Montgomery soils. This is due to some obscure cause which may become apparent when similar studies are extended to other areas.

Another source from which data were obtained consisted of the records maintained for revenue purposes. Two large wheat-growing areas were selected. In this case, instead of the degree of alkalization being determined, the pH values of the soils were obtained, since the pH value increases with the increase in the degree of

alkalization. No actual yield measurements were made, but were taken from the farmers or the revenue records. The correlation coefficient between the yield of wheat and pH value was found to be 0.51, which was significant. These results are recorded merely to stimulate further research in this direction. The actual yield values being unreliable, a higher correlation could not be expected. The important point is that the correlation is significant.

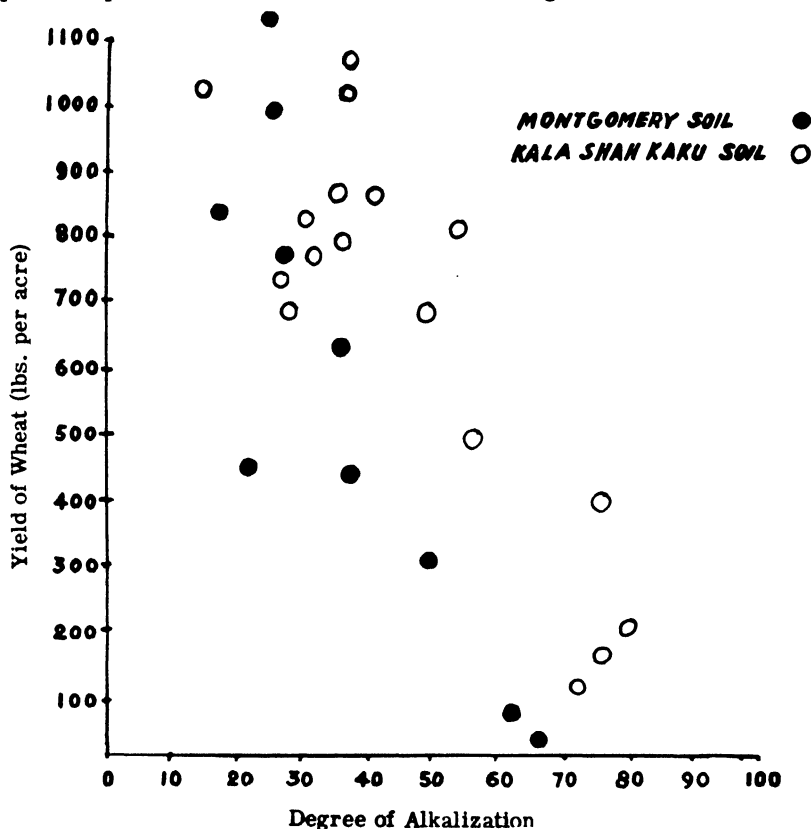
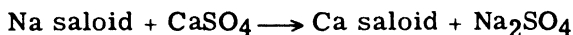



Fig. 33. Relation between D.A. and Yield of Wheat

A further confirmation of these indications was afforded by the examination of the rice soils in certain areas. In this case also, a significant correlation was found to exist between the yield of rice and the pH value: the higher the pH value, the lower the yield of rice. It was noted that average yield begins to go down when the pH values increase beyond 8.5. The importance of pH value in the studies of the saloids must be emphasized. We can have a mixture of Na-Ca saloids with a pH value below 8.5. Such a soil will not depress the crop yield. Therefore, a certain amount of tolerance for Na saloid by crops is indicated. It is only when this limit of tolerance is exceeded that crop yield begins to decrease. This apparently happens when the pH value is higher than 8.5.

Soil Alkalinity and Reclamation

Since Na saloid is the limiting factor as regards crop yield in alkaline soils, the reclamation of such soils must involve the conversion of Na saloid to Ca saloid. The simplest method of accomplishing this would appear to be leaching it with a Ca salt. The cheapest Ca salt and the one most extensively used for the purpose is $CaSO_4$. The chemical reaction that takes place is

$$\text{Na saloid} + CaSO_4 \longrightarrow \text{Ca saloid} + Na_2SO_4$$

The $NaSO_4$ thus formed is leached downward and drained away. As the Ca saloid forms at the surface and then gradually moves downward, the vegetation begins to take root, of which common grass is the first to appear. The roots of the grass open up the soil as they grow. The roots of plants also give out carbonic acid, which further helps to neutralize the alkalinity. If the pH value of the soil was as high as 10.5, it would drop to as low as 9 near the roots, and at that stage a rice crop could be sown. Once a rice crop is established, further process of reclamation is accelerated.

This is a brief outline of the method of reclamation. We shall now take up the scientific principles involved in the conversion of the Na saloid into Ca saloid and vice versa. The problem is not merely the reclamation of alkaline soils, but also prevention of the formation of Na saloid in areas where artificial irrigation is practiced and the waters contain appreciable amounts of Na salts which gradually lead to the formation of Na saloid.

From a consideration of the reactions involved in the system Na salts – Ca salts – Na-Ca saloids, it seemed probably on the face of it that for every concentration of Na ions in solution there must be a corresponding concentration of Ca ions which would prevent the formation of Na saloid. If such were the case it follows that the addition of Ca salts to the irrigation water would prevent the formation of Na saloid. This would be of considerable importance both in controlling the deterioration and in the reclamation of land in which Na saloid had accumulated. From a further consideration of the system Na-Ca salts – Na-Ca saloids, it would also appear that for each ratio of the latter there must be an equilibrium concentration of Na-Ca ions in solution. It follows from this that the question of the salt concentration permissible in an irrigation water must have some relation to the quality of the soil to be irrigated. For instance, a soil with a high degree of alkalization is unlikely to deteriorate further when irrigated with water which would cause the deterioration of soil with a low degree of alkalization. In what follows an account is given of the experimental work designed to study the reactions involved in the system mentioned.

So that the reactions might be studied over a wide range, a black cotton soil which contained 52% of clay was selected. It also contained about 10% calcium carbonate and a little over 60 milliequivalents of Ca saloid per 100 grams. Ten-gram portions of the soil

were leached with 1000 cc of NaCl solution of increasing concentration in 100-cc lots. The amount of total Ca in the leachate was determined. The results, plotted in Figure 34, show that increasing concentrations of NaCl bring out increasing amounts of Ca. The relation, however, is not linear but logarithmic, and resembles an adsorption isotherm.

Since the soil contains about 10 per cent $CaCO_3$, some of the Ca in the leachate must have come from this source. In order to elim-

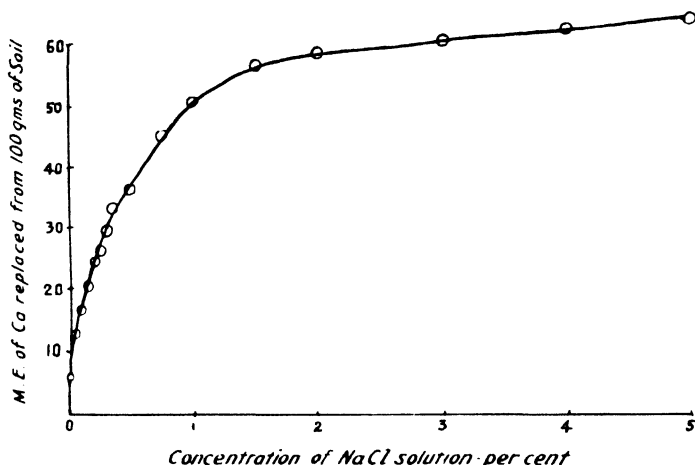



Fig. 34. Relation between Concentration of NaCl Solution and the Replacement of Ca from the Soil

Table 22. Replacement of Ca by Na on leaching as well as single treatment with NaCl.

Conc. of NaCl (%)	m.e. of Ca replaced from 10 gm. of soil by 1000cc. NaCl sol'n.		Ratio Na/Ca
	Leaching	Single treatment	
0.00	0.490	0.3185	....
0.05	1.370	0.9065	4.85
0.10	1.665	1.2490	7.31
0.15	2.204	1.4700	9.47
0.20	2.600	1.7391	10.74
0.25	3.240	2.0335	11.53
0.30	3.970	2.3030	12.26

inate this effect the soil was first converted to the acidoid and then to Ca saloid by the addition of $Ca(OH)_2$. This derived soil contained 58.016 m.e. of Ca saloid per 100 grams.

Ten-gram portions of this soil were leached with 1000 cc of NaCl solution of increasing concentration in 1000-cc lots and Ca determined in the entire leachate. In another experiment 10-gram portions of the soil were shaken for two hours with 1000 cc of NaCl solutions of increasing concentration. The results of both the leach-

ing experiment and single treatment are given in Table 22. Also included is a column which gives the ratio of Na to Ca at the equilibrium point for the various concentrations of NaCl employed for the single treatment. It will be seen that this ratio is not constant, but increases with increasing concentration of NaCl. In other words, as the concentration of NaCl increases, a relatively smaller amount of Ca is required to prevent its action with the soil as regards conversion of Ca into Na saloid.

In the experiments already described, the course of the conversion of Ca into Na saloid was followed by estimating the replaced Ca and assuming that the Ca replaced was equivalent to the Na saloid formed. In what follows, Na saloid was determined directly by the $(NH_4)_2CO_3$ method described previously.

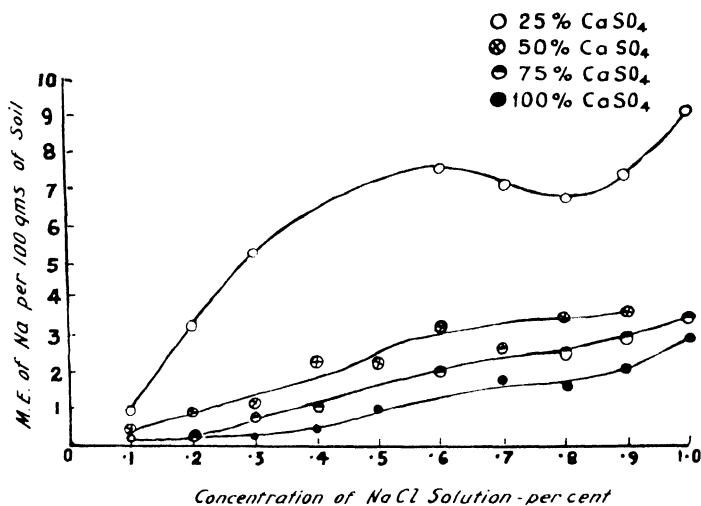



Fig. 35. Replacement of Na Ions by Ca by Leaching with NaCl Solution Containing Different Amounts of $CaSO_4$

Having determined the equilibrium point in the system NaCl-Ca-Na saloid, the alterations caused in this system by the presence of Ca salts were next studied. Ten-gram portions of the soil were leached with 1000 cc of NaCl solution of increasing concentration and containing Ca salts. The experiment was divided into six series with solutions of increasing amounts of $CaSO_4$ and also in one case a solution saturated with $CaCO_3$. Calcium sulphate was preferred as the source of Ca ions because from the practical point of view this is the only salt that can be applied economically on a field scale. The results are plotted in Figure 35.

The concentrations of Ca ions are compiled in terms of a saturated solution of $CaSO_4$, which is N/25. The results show that a saturated solution of $CaSO_4$ can prevent the formation of Na saloid by a solution containing as much as 300 to 400 parts per 100,000 of NaCl.

The results shown in Figure 35 are of great practical value, as they

indicate that there is no necessity to use a more soluble salt of Ca for the reclamation of alkaline soils; the concentration of Ca ions given by a saturated solution of $CaSO_4$ is quite sufficient to bring about the necessary conversion of Na into Ca saloid. This fact was confirmed by a more direct experiment, as follows.

A composite sample was prepared from a number of alkaline soils. This sample was leached in 10-gram portions with NaCl solutions of increasing concentration with different amounts of $CaSO_4$. Sodium saloid was determined in the soil after leaching the original soil containing 11.05 m.e. per 100 grams of soil. The results given in Table 23 bring out the interesting fact that it is possible to reclaim an alkaline soil even with a NaCl solution of as high a concentration as 5 to 6 hundred parts per hundred thousand. It is to be noted that $CaSO_4$ solution, even at 50% saturation, has considerably reduced the amount of Na saloid in the soil. It is clear, therefore, that unless the concentration of Na ions is so high as to

Table 23. Replacement of Na ions by Ca from a composite sample of alkaline soils by leaching with NaCl solution containing different amounts of $CaSO_4$

Con. of NaCl (%)	Na saloid formed (m.e. per 100gm. soil)			
	$CaSO_4$ 25%	50%	75%	100% Saturation
0.10	1.00	0.50	0.20	0.40
0.20	3.30	1.10	0.20	0.30
0.30	5.30	1.40	0.80	0.30
0.40	4.50	2.40	1.00	0.50
0.50	5.30	2.20	2.00	0.90
0.60	7.60	3.20	1.90	2.00
0.70	6.95	2.60	......	1.80
0.80	6.76	3.40	2.50	1.60
0.90	7.30	3.60	2.80	2.00
1.00	9.00	......	3.40	2.80

cause direct injury to plants, the bad effect of Na ions on soils can be greatly reduced by introducing $CaSO_4$. The important point in deciding the quality of irrigation water is determination of the Na/Ca ratio, not merely the total saloids.

These results also explain a certain anomaly in the behavior of different saline soils. For instance, it is known that some of them can be reclaimed by simple leaching with water, whereas others get worse when subjected to leaching. In the light of these experiments it appears logical to conclude that soils containing an excessive amount of Na salts may be in a flocculated condition and pervious to water; but the leaching of such a soil must be done carefully, because as soon as the excess salt is removed, the soil will become dispersed and impervious to water. On the other hand, if the soil contains Ca as well as Na salts, the leaching process does not bring about the accumulation of Na ions, provided there are enough Ca ions to offset the effect of the Na salts. Such a soil would be easy to reclaim and would need no treatment beyond leach-

ing. It is, therefore, of great importance in all studies of saline soils to examine the calcium of the water extract to see if a sufficient quantity is present to counteract the effect of sodium ions, in which case one can go ahead with leaching. If on the other hand, sufficient calcium salts are not present, they must be added, in the form of $CaSO_4$. However, the important point is that the addition of $CaSO_4$ must be done simultaneously with the leaching operation, so that conditions are created by virtue of which the formation of sodium saloid is prevented.

The results mentioned above lead to a conclusion of great practical importance. Hitherto the use of $CaSO_4$ has been confined to land reclamation; as a preventive measure against soil deterioration its value has not been recognized. Soils in certain areas are slowly deteriorating; but this can be prevented to a large extent by the use of $CaSO_4$ as a manure. The need for this application will appear when the degree of alkalization rises above 20%, or when the pH value is higher than 8.5. If at this stage $CaSO_4$ is applied, the presence of Ca salts will prevent any further formation of Na saloids that might be taking place.

From field experiments on the effect of $CaSO_4$ on alkaline soils, it has been found that even under the worst alkalizing conditions it is useless to apply $CaSO_4$ at the rate of more than 2 tons per acre. From this it follows that in the early stages of soil deterioration a much lighter dressing of $CaSO_4$ would be adequate. The exact amount and the frequency of application would of course depend on the stage of deterioration – a condition which could be easily determined by an examination of the soil.

Alkaline soils usually contain a large percentage of soluble alkali salts. Thus some confusion arises as to the exact meaning to be attached to the terms "alkaline" and "saline" soils. The Russian terms solonchak and solonetz are probably more precise in this respect. Saline soils, for convenience of reference, may be defined as those having an excessive amount of soluble Na salts. By an excessive amount is meant an amount which has rendered the soil barren, so that the cause of barrenness can be directly attributed to salinity. Alkaline soils may be defined as those having an excessive amount of Na saloids, or a degree of alkalization above 20%, or a pH value above 8.5. It is true that there is a good deal of overlapping of saline and alkaline soils, but generally there is no difficulty in deciding which of the two characteristics dominates. However, there are some soils which must be described as saline-alkaline soils, because the salinity and alkalinity in them is so excessive that it is neither possible nor useful to decide which of the two dominates. According to these definitions certain broad generalizations may be made which will be helpful in dealing with such soils.

(a) All alkaline soils contain Na saloids, but all soils containing Na saloids are not necessarily alkaline. The essential condition of

an alkaline soil is that it must yield an appreciable amount of NaOH on hydrolysis in contact with water. The real effect of hydrolysis becomes apparent only when the hydrolyzed clay yields a solution above pH 8.5, and it is only above this pH value that its harmful effect on vegetation begins to be evident.

(b) Saline soils develop into alkaline soils only if the soluble salts do not include $CaSO_4$ or $CaCl_2$. If either of these salts is present in sufficient amount, simple leaching will result in a normal soil. In the reclamation of saline soils it is important to bear this in mind.

(c) In some soils it is not possible to determine which of the two factors (namely, salinity or alkalinity) predominates. Such soils must be designated as saline-alkaline soils.

To avoid confusion the Russian terms solonchak and solonetz must be considered synonymous with saline and alkaline soils, respectively.

Before starting the reclamation of saline-alkaline soils a knowledge of the following is essential:

(a) Quality of the soil.

(b) Quality of the proposed irrigation water.

(c) Nature and distribution of salts in the soil profile.

The most important point in judging the quality of soil from the reclamation point of view is its degree of alkalization or the amount of Na saloid in it. The higher the degree of alkalization the greater will be the difficulty in reclaiming it.

The quality of water is not so important from the point of view of actual reclamation because, as shown above, a soil can be reclaimed even with water containing 500 parts per 100,000 of NaCl provided the necessary quantity of Ca salts are present; but subsequent irrigation must be done with water whose total solids does not exceed the prescribed limit. The presence of Ca salts in water to be used for reclamation is very necessary, and this can be assured by applying $CaSO_4$, or by introducing it in the irrigation water.

A study of the soil profile affords valuable help in reclamation work. For instance, if Ca salts (other than $CaCO_3$) are present, reclamation will be easy. If the soil is impervious to begin with, as frequently happens with alkaline soils, surface washing should be resorted to. The water in this case should be drained off when its pH value rises approximately to that of the soil as determined in the laboratory.

CHAPTER XIV

THE QUALITY OF IRRIGATION WATERS

Purely from the point of view of its effect on soils, information regarding any water used for irrigation is essential on:

(a) total soluble salts;

(b) ratio of Na to Ca in the solution;

(c) nature of the soil to be irrigated.

By taking into consideration the normal amount of $CaCO_3$ that can be expected to be brought into solution when irrigation water is applied to a soil containing $CaCO_3$, we can find the minimum concentration of Na salts in an irrigation water which will not result in the gradual replacement of Ca by Na. The logic of this will be apparent from the fact that most of the soils of this type contain $CaCO_3$, with which the irrigation water will become saturated as soon as it is applied to the field.

The Salt Index

The solubility of $CaCO_3$ in water depends on the partial pressure of CO_2 in the atmosphere surrounding it. The normal concentration of CO_2 in soil air to a depth of 15 cm is 0.3%, though it may rise to 1% or more, especially in wet soils rich in humus. The partial pressure of CO_2 at 0.3% concentration is 2.18 mm, or $2.18/760 = 0.00278$ atmosphere. The solubility of $CaCO_3$ at this partial pressure of CO_2 is 0.0126 per cent, or 12.6 parts per 100,000. Reference to Table 24 will show that the minimum concentration of Na ions that is in equilibrium with a given concentration of Ca is 4.85 times the concentration of Ca ions. In other words, 12.6 parts per 100,000 of $CaCO_3$ will be in equilibrium with $12.6 \times 40/100 \times 4.85 \times 58.6/23 - 62.2$ parts per 100,000 of NaCl, or 75.4 parts per 100,000 of $NaSO_4$. Therefore in the absence of Ca salts the total salts in an irrigation water should not exceed 62 to 75 parts per 100,000 of NaCl or $NaSO_4$, respectively, or the Na ions should not exceed 24.5 parts per 100,000. If on the other hand, some $CaSO_4$ or $CaCl_2$ (but not $CaCO_3$) is present, a correspondingly larger amount of Na ions can be tolerated.

The following general formula for expressing the quality of water by a concrete value has been derived. The value given by this

formula has been designated the salt index. All quantities in the formula refer to parts per 100,000:

$$\text{salt index} = (\text{total Na} - 24.5) - [(\text{total Ca} - \text{Ca in } CaCO_3) \times 4.85]$$

The salt index is negative for all good waters and positive for those unsuitable for irrigation purposes. The degree of badness may be reckoned as equivalent to the magnitude of this positive factor, and the degree of goodness as equivalent to the magnitude of the negative factor. In this way it is possible to build up a scale for irrigation waters. The salt index will vary from −24.5 to zero for all good waters, and from zero up to any positive value for all bad waters. On this scale distilled water has a salt index of −24.5.

The actual determination of salt index is carried out by estimating the following in the sample of water:

sodium sulphate
sodium chloride
sodium carbonate, or bicarbonate
calcium carbonate
calcium sulphate or chloride

The usual convention for the combination of ions is, of course, observed. Magnesium is rarely found, but if present, it should be reckoned as calcium for the purpose of calculating salt index.

The criteria stated above are quite satisfactory in the absence of any knowledge about the soil which a particular water has to irrigate, and any water with a positive salt index can be rejected on that basis. An examination of the soil, however, might render a water with a positive salt index fit for irrigation. For instance, if the soil contains $CaSO_4$ or $CaCl_2$, a higher salt index could be tolerated than otherwise. It is also possible that the former may be available in large quantities and could be applied to the soil or added to the irrigation water, thus lowering its salt index.

There is a third possibility, i.e., that the soil is already in a partially deteriorated condition and since these reactions obey the law of mass action, further deterioration will not take place. In other words, if the soil already contains some Na saloid, a certain water, though bad for a normal soil, may not make this particular soil any worse.

The next question is, What is the upper limit beyond which the water must be rejected as entirely unfit for irrigation purposes, whatever the state of soil it is going to irrigate? The greatest tolerance of NaCl for plants is 0.20 mol, or 117 parts per 100,000, though this amount may be increased tenfold in the presence of Ca salts. We have also seen that in the presence of $CaSO_4$ up to 50 per cent saturation, the amount of NaCl may be raised to 150 parts per 100,000 without causing an accumulation of Na saloid. It appears that to be on the safe side a water should be totally rejected for irrigation purposes if the concentration of NaCl in it exceeds 117 parts per 100,000 or, reckoned as sodium, 46 parts per 100,000.

CHAPTER XV

SOIL PERMEABILITY

Although from the agricultural point of view soils containing Na saloids possess some of the worst features, they have certain desirable properties for other purposes. For instance, Na saloid goes into suspension immediately on coming into contact with water. The fine clay particles thus produced fill up all the interstices and the soil is rendered impervious to water. In this respect its properties are the reverse of Ca saloid. These properties, which are bad from the agricultural standpoint, are of considerable value when a material for lining canals to reduce seepage losses is required. We have already seen that the conversion of a Ca saloid into a Na saloid is an easy matter; all that we have to do is to estimate the amount of Ca saloid and add an equivalent amount of $NaCO_3$ to it, when the Ca saloid is quantitatively converted into a Na saloid.

Before describing the practical details of using this method in the field, it is desirable to give details of the laboratory experiments designed to study the reduction in permeability of soils treated with $NaCO_3$. Incidentally the experiments will afford an insight into the methods of testing the suitability of a soil or a channel for the sodium carbonate treatment. The chief factors determining the permeability of a soil to water are its clay content and the relative amounts of Na-Ca saloids in it. These can be determined easily. The most important determination relating to the present discussion is the measurement of permeability. The chief difficulty in such measurements lies in the fact that there is no satisfactory method of packing the soil, and as the results are very largely affected by the manner of packing, they are not reproducible. The problem of packing, however, can be solved by allowing the soil to pack itself in a special brass percolating cylinder, which is 2.5 inches in diameter and is provided with a stout flange at the bottom; against this flange is held a perforated brass disc, the other side of which is held to the flange of a funnel. The joint between the cylinder and the perforated disc is made water-tight by rubber washers. A filter paper is interposed between the cylinder and the perforated disc. The whole apparatus together with the funnel is secured with bolts.

Twenty-five grams of the soil are left with about 250 cc of water overnight, after stirring once. The following morning the suspen-

sion is transferred to a measuring flask and the total volume made up to 500 cc. The suspension is brought to a uniform consistency by gently shaking the flask. The total suspension is then transferred to the percolating cylinder. Percolation starts almost immediately and continues at a gradually diminishing rate. After every hour (sooner if the volume of the percolate is more than 100 cc), the clean filtrate is gently poured back into the cylinder. After about 5 or 6 hours the rate of percolation becomes almost constant. The volume of percolate collected in unit time, or some factor related to it, is taken as the measure of permeability.

For purposes of comparison and for studying the effect of $NaCO_3$ this simple device serves quite well. In Table 24 are given the results of permeability tests with a number of soils. It will be seen that the rate of percolation expressed in cc per hour is reduced by 40 to 90% of the original value when $NaCO_3$ equivalent to the Ca saloid in the soil is added.

Table 24. Permeability of soils with and without sodium carbonate treatment

Soil No. R.M.	Clay (%)	percolation (c.c. per hr.) Treated	Untreated	% reduction
5	4.5	106	27.0	74.5
6	10.5	68	19.5	71.3
7	32.0	65	3.2	95.1
8	20.2	138	14.5	89.5
9	5.4	125	13.0	89.6

The method described is suitable for ordinary measurements, but it has some obvious disadvantages. One rather serious drawback is that when dealing with highly dispersed soils, especially the $NaCO_3$-treated ones, the fine clay particles are likely to choke the filter paper at the bottom, resulting in a greatly reduced rate of percolation which may not reflect the actual state of the soil, but gives an exaggerated picture of the reduction in permeability. This defect was removed by placing the soil between sand layers. The soil layer was 1 inch thick, which necessitated the use of a larger head of water. The arrangement finally adopted also enabled the examination to be made of soil from a canal bed in the wet state without disturbing it. The percolating cylinder shown in Figure 36 is of the type described, except that it is made in three sections.

The middle section, which is 1 inch long, contains the soil; the lower section is filled with sand; the middle section with the wet soil block is placed on it and the top section then placed in position. The two rubber washers keep the joints leak-tight and the various sections are clamped together, after which some sand forming a layer of almost 1 inch is spread on the soil. The top of the cylinder is closed with a brass cap with two holes, one connected to the water

reservoir and the other to a tap which is opened during the filling of the cylinder and closed when the cylinder is full. The water reservoir can be raised or lowered and is kept at a constant level with the help of an overflow arrangement. Several percolating cylinders can be run at a time, every unit working at the same pressure head.

The rate of percolation is determined by measuring the volume of the percolate in a given time. A standard head of 10 feet of

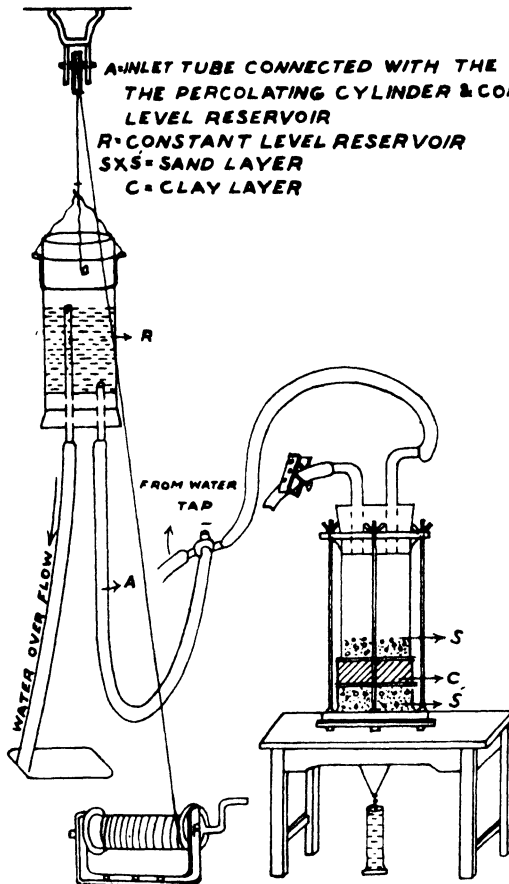



Fig. 36. Diagram of the Percolating Cylinder and Constant Level Arrangement

water is maintained for all measurements and the results are computed in cusecs per million square feet of surface simply by multiplying the number of cc of percolate collected in one hour by 0.30. Obviously this factor applies only to a cylinder of 2.5-inch diameter. The thickness of the soil block (1 inch in this case) and the pressure head must be specified when reporting the results. Assuming that the rate of percolation is proportional to the pressure head and the thickness of the soil block, we can define the permeability of a canal bed in cusecs per million square feet of surface for a thickness of

1 foot under a pressure of 1 foot of water. This is the conventional way in which irrigation engineers like to express the seepage loss in canals. In Table 25 are recorded results of permeability measurements on soil blocks from the various parts of a canal (Kasur Branch Lower).

Table 25. Permeability of material forming the bed of a canal at certain reaches

Locality R.D.	Clay (%)	Permeability in cusecs per million sq. ft.
46,000	10.4	0.59
53,000	4.0	192.75
55,000	10.9	0.015
56,000	9.2	0.035
57,000	12.4	0.075
58,000	9.7	0.035
59,000	12.2	0.010

It will be seen that at R.D. 53,000 the permeability is over twelve thousand times that at R.D. 55,000. By examination of the soil below the bed of a canal, it is possible to indicate the reaches in which seepage is high and which it will pay to treat with sodium carbonate. The following method is employed for taking undisturbed samples of canal bed earth. A core sampler consisting of a brass cylinder of exactly the same diameter as the percolation cylinder is pressed into the clay bed after removing the silt overlying it. The sample is then pressed out of the core sampler directly into the middle section of the percolation cylinder, which is then closed on both sides by closely fitting lids. The sample is brought to the laboratory and examined directly after clamping to the percolating cylinder as usual.

Canal Seepage Losses

Large-scale experiments to explore the possibility of preventing seepage losses from canals by the use of sodium carbonate were started in the first instance to gain experience in the use of this chemical and to discover the best way of applying the method in practice.

The sodium carbonate method was first tried in two channels: a 100-foot length in each distributary was enclosed in brick walls and the rate of fall in the water level was taken at regular intervals. This gave a measure of the seepage loss. Sodium carbonate was then added to give a 0.1 per cent solution, and its effect on the seepage loss noted. The results were encouraging in both cases. The seepage loss was reduced by 50 per cent in one case and by 45 per cent in the other during the course of 4 days. The practical difficulty of applying the material in the form of a solution is obvious. The maximum effect cannot be expected unless all the solution reacts with the bed material.

Two compartments 100 feet long were made with a space of 50 feet between them in a channel 12 feet wide by 2 feet deep. The partitions were of brick and cement, strengthened with a backing of earthwork. The tanks were filled every day and seepage losses measured over a period of five days. After this one of the tanks was emptied and refilled after applying sodium carbonate to the bed. Twenty-four-hour seepage losses were again measured for five days. Thus by taking measurements of the same tank before and after treatment, variations due to differences in the soil bed were eliminated. This is an important point; seepage losses from an entire canal or distributary cannot be measured by the compartment method, for the results will be applicable only to that portion of the canal in which the compartment may be situated. In this experiment a decrease of almost 40% in seepage loss was shown. Soil samples taken in the bed of the channel in 1-inch sections after the sodium carbonate treatment showed that the alkali had penetrated to a depth of 3 inches below the broadcasting surface. The procedure adopted for applying the sodium carbonate was to remove six inches of the bed silt and broadcast 2 cwt of sodium carbonate on the surface as evenly as possible. The bed silt was then put back to cover it. The bed of the channel consisted of stiff soil containing 20 to 30 per cent of clay.

In order to test the treatment under running canal conditions the Awagat distributary of the Lower Chenab Canal was selected. The behavior of this distributary before treatment was known and hence afforded a readily available basis of comparison after treatment. The authorized full supply of the channel was 54 cusecs, but in order to feed the tail the supply at the head had to be increased to 58 cusecs. Even with this discharge some difficulty was felt at the tail.

In order to develop the field technique for the treatment, an experimental reach of about 7000 feet was treated during a closure. The procedure adopted was as follows. The bed was dug to a depth of 1 foot below its level. The silt thus removed was dumped on both sides. The side slopes of the excavated portion were kept as nearly vertical as possible, so that the maximum bed width could be treated. A layer of earth 2 inches thick obtained from the neighboring land was placed on the bed. This earth had been examined in the laboratory to make sure that it was suitable for the purpose. The earth was finely powdered with mallets, dressed and thoroughly rolled with hand rollers.

The unit of treatment was a 10-foot length of the channel. A solution of $NaCO_3$ containing 6.6 pounds of $NaCO_3$ per cubic foot of water was prepared. This was sufficient for the treatment of 33 cubic feet of soil, or 200 square feet when spread in the channel bed. The solution of $NaCO_3$ was sprayed uniformly from watering cans on the surface of the 2-inch layer of earth. After treating this layer, a second layer of earth also 2 inches thick was laid on the treated surface. This second layer was rolled and treated with the

solution of $NaCO_3$ in a manner similar to the first. After treatment the earth layer was covered by an 8-inch layer of silt dug from the channel, to restore the bed to its original level.

After the channel had been running for about three months, the bed was examined and it was found that the sandwiched earth layer was not disturbed. This showed that the technique adopted was satisfactory. Therefore the entire length of about 13 miles was subjected to a similar treatment. When the distributary was reopened after the second treatment, the authorized full supply of 54 cusecs was admitted at the head. With this discharge running it was found that the tail could be supplied without difficulty. Actual measurements showed that there was a saving of 2.3 cusecs of water which was previously lost by seepage. This would mean that the entire cost of treatment would be recovered in three years.

In making trials of the effectiveness of the sodium carbonate treatment, the channel selected should satisfy the following conditions:

(1) It should have a meter at the head, a carefully calibrated tail, and preferably one or two meters between its head and tail.

(2) The excessive seepage losses in the channel should be an established fact as distinguished from other losses such as overdrawing outlets.

(3) The outlets should be of the latest type so as to admit correct calculation of discharge.

CHAPTER XVI

DISPERSION OF SODIUM SALOID IN WATER

Auto-Disintegration

One of the outstanding properties of sodium saloids is their ability to go into suspension without any mechanical shaking. This phenomenon, known as auto-disintegration, is characteristic of lithium saloids also. The latter are of theoretical interest; attention may, therefore, be directed to the examination of Na saloids only with respect to this property.

Since auto-disintegration is shown only by Na saloid in natural soils, it has some correlation with the degree of alkalization. A quantitative estimate of this property can be made by determining clay in a soil by auto-disintegration, without any shaking (dispersion factor, or D.F.) and expressing it as a percentage of the total clay. This ratio is called dispersion coefficient, or D.C.

The effect of the gradual neutralization of soil acidoid by NaOH on its dispersion coefficient was studied on four soils differing widely in character. The four soils chosen were P.C. 6, a yellow lateritic soil; P.C. 13, a black cotton soil; P.C. 15, a red ferruginous soil; and P.C. 123, an alluvial clay sub-soil. These soils were first converted into the acidoid and then gradually neutralized to different pH values with NaOH and their dispersion coefficients measured both by auto-disintegration and shaking for 24 hours. The results are shown graphically in Figure 37, from which the following conclusions are drawn.

(1) The maximum dispersion both by auto-disintegration and by shaking is attained at pH 10.8, but the manner of approach to this maximum is different for different soils.

(2) The change in dispersion with increasing pH value is very slight up to pH 6 in the case of P.C. 6 and P.C. 13 soils. This is followed by a rapid change, which again slows down toward the approach of the maximum value.

(3) Soil P.C. 123 shows very little dispersion up to pH 10, after which the curve shoots up rapidly and the maximum is reached at pH 10.75.

(4) Soil P.C. 15 is somewhat similar to P.C. 123 as regards auto-disintegration, but resembles P.C. 6 and 13 when dispersion is produced by shaking.

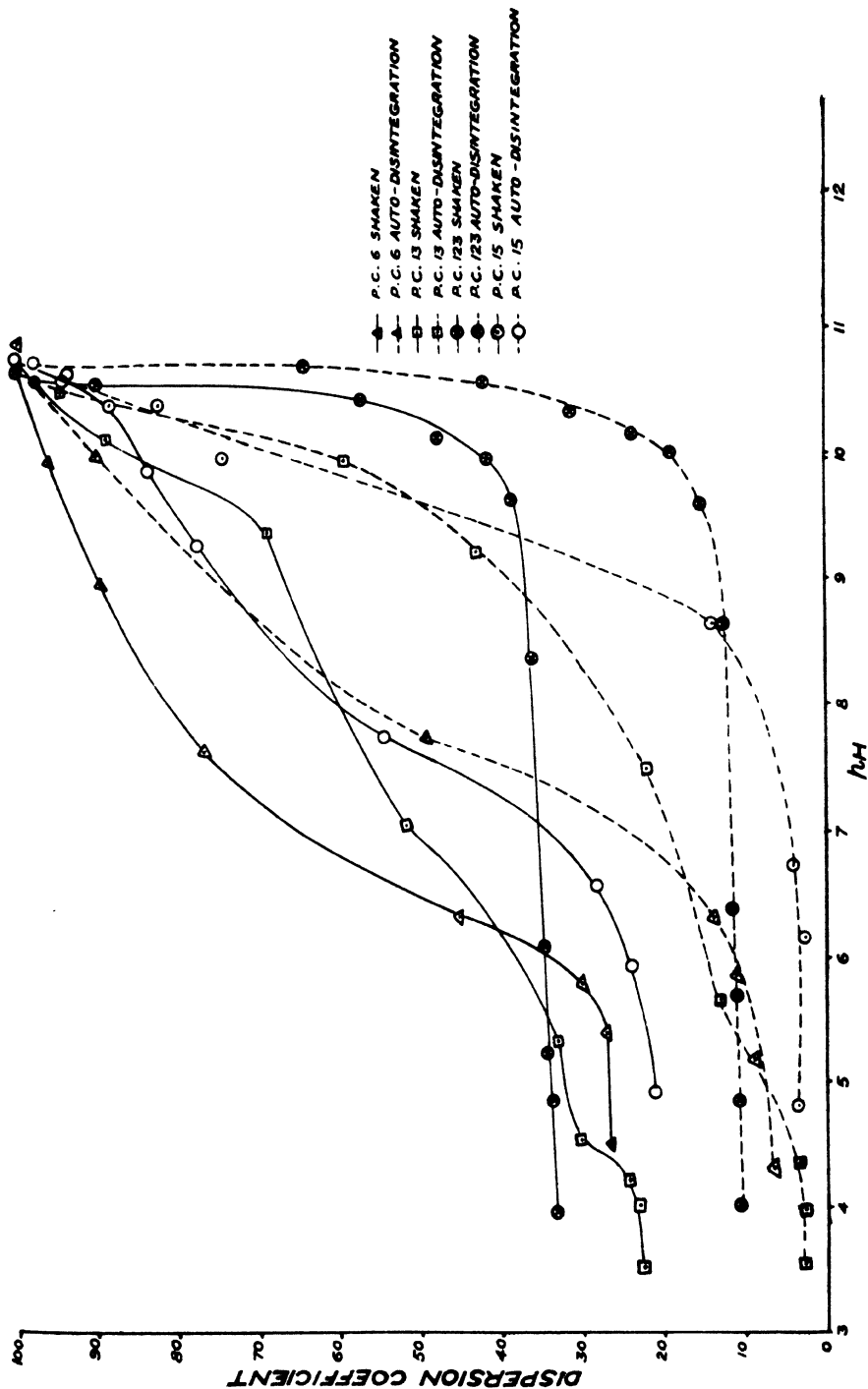



Fig. 37. Effect of pH Value on the Dispersion of H Soils with NaOH

(5) The change in the shape of the pH-dispersion curve occurs at a lower pH value with shaking than with auto-disintegration; otherwise the general characters of the curves are the same for the two methods. Shaking merely helps the disruptive forces and brings about disintegration at a lower pH value.

In order to see if all Na soils show the maximum dispersion by auto-disintegration and to determine how this value compares with mechanical shaking in the case of different types of soils, 74 soils were examined. All were first converted into H soils as usual by acid treatment, and dried. They were then neutralized to pH 10.8 with NaOH and the clay content determined by shaking for 24 hours in a mechanical shaker and by auto-disintegration, i.e., without any shaking for the same time. Since the actual values are not of much interest, the difference between the clay obtained by shaking and by auto-disintegration is shown in Table 26 compared with the number of soils that show a difference of that magnitude.

Table 26. Difference between the clay contents obtained by auto-disintegration and by shaking in 72 soils neutralized to pH 10.8 with WaOH after acid treatment.

Difference in clay (%)	Number of soils showing difference of that order
6	1
3	7
2	11
1	18
Less than 1	35

It is rather interesting that in one solitary case where the difference is almost 6 per cent the value by auto-disintegration was 46.56 and by shaking 40.12. This value was not repeated and might be due to some error in manipulation. The important point that emerges from this study is that though the soils used belonged to different types, including black cotton, lateritic, red ferruginous, alluvial, and humus and had been collected from different localities, not a single one failed to show maximum dispersion by auto-disintegration. We may thus state the general conclusion that all Na soils at pH 10.8 go into suspension by auto-disintegration, without any mechanical shaking. The importance of this conclusion will be discussed later when dealing with the mechanical analysis of soils.

Some interesting questions arise from the fact that dispersion is complete and at its maximum when the pH value of a H soil is made equal to 10.8 by the addition of NaOH or LiOH, for example, whether the soil at different pH values, which is not at its maximum dispersion, represents a stable structure or whether it is merely a question of time? It is quite likely that the rate of dispersion of a Na soil at different pH values may be different, in which case it would be more helpful to measure the rate of dispersion. The development

of the chainohydrometer for the mechanical analysis of soils (described later) has made this study possible, because the same suspension could be examined at different time intervals, which could not have been done with the pipette method.

Rate of Dispersion and pH

Increasing amounts of NaOH were added to a 2% suspension of H soil (P.C. 13). Particles of 0.005 mm diameter were determined at various intervals of time. The results are given in Table 27. The readings were continued for 50 days, after which the suspensions were heated for 10 hours at 60 to 70°C. It will be seen that differences due to pH values are maintained throughout. There is, however, a slight tendency for the dispersion to increase during the first 5 to 7 days up to pH 10 or more. Dispersion at higher pH

Table 27. Rate of dispersion of H soil neutralized to different pH levels.

*pH	Per cent (0.005mm.) particles after keeping for various intervals of time													
	4 hrs.	8 hrs.	12 hrs.	24 hrs.	2 days	3 days	4 days	5 days	6 days	7 days	14 days	30 days	50 days	50 days then heated for 10 hrs.
5.90	6.2	7.6	6.5	6.2	8.4	8.3	9.8	9.4	9.6	9.5	9.5	11.6	12.7	12.7
6.62	9.6	9.7	10.0	10.3	11.7	12.5	13.4	13.2	13.7	14.3	16.6	17.4	19.2	21.2
7.71	12.9	13.2	13.0	14.3	14.8	15.9	19.1	18.6	18.9	19.6	23.8	25.2	28.0	29.4
7.92	15.3	15.6	15.9	18.5	20.4	21.1	21.6	22.3	23.0	23.5	25.4	27.6	29.1	31.0
8.60	14.9	15.4	16.9	21.7	22.9	23.9	24.1	24.9	26.7	27.3	28.7	32.7	34.4	34.9
9.26	16.6	18.7	21.0	23.1	26.0	27.9	28.2	28.8	30.9	31.0	31.3	33.4	35.8	36.2
9.60	18.8	21.6	23.7	26.7	29.4	31.5	31.9	32.6	32.6	34.1	35.3	36.3	38.0	38.4
9.92	24.6	30.8	34.1	38.7	41.4	42.6	43.0	44.1	45.6	45.8	46.1	47.2	47.2	47.5
10.52	60.5	60.9	60.7	61.3	61.1	62.9	62.7	61.0	60.8	60.3	59.7	60.5	59.7	60.6
10.95	64.2	64.6	65.2	62.3	63.0	62.9	61.9	62.2	61.6	61.2	60.9	61.2	61.6	62.3

values seems to have reached a maximum value in four days. It is clear that soils at different pH values represent structures which, if not permanent, are at least water-stable for a considerable length of time; not even heating makes any appreciable difference.

In order to see if this state of aggregation is confined to the clay fraction or extends to the entire soil including the coarser fractions, complete mechanical analyses up to 0.06-mm particles were made after leaving the suspensions neutralized to different pH values for 3 weeks. The results, given in Table 28, show that the relation between pH and dispersion is the same whatever particle size is taken into consideration. In other words, the alkali affects all the fractions equally.

To compare the dispersion of Na saloid with saloids of other metals, increasing amounts of various hydroxides were added to H soil (P.C. 13) and dispersion measured at every step by determining particles of 0.005-mm diameter with the chainohydrometer. The total quantity of alkali in this case was pushed much beyond the base equivalent limit. For instance, the H soil required approximately 60 to 70 cc of N alkali for 50 grams to bring it to pH 10.8.

When more alkali is added, a slight increase in dispersion is noted, which continues until flocculation takes place. This slight increase is most probably due to the partial breakdown of the aluminum silicates with the formation of aluminates. It might be pointed out that the quantity of alkali added was subtracted from the weight of

Table 28. Complete mechanical analysis of a soil at different pH values (after 3 weeks' standing)

pH	m.e. of NaOH added to 50 gm. of soil	0.06 mm.	0.04 mm.	0.02 mm.	0.01 mm.	0.008 mm.	0.005 mm.	0.002 mm.
5.55	6	58.0	52.0	37.5	31.6	30.4	27.7	23.5
6.16	15	66.3	59.2	51.4	42.6	39.4	36.3	31.3
6.60	20	68.0	64.4	54.3	45.8	43.6	38.4	35.0
7.15	24	71.8	68.0	55.0	47.2	46.9	42.2	37.5
7.45	28	72.9	69.1	59.7	51.2	48.7	44.8	39.6
8.25	34	79.3	73.8	66.2	54.1	51.7	47.3	43.2
9.40	40	83.0	81.3	68.9	57.5	56.5	51.5	44.3
9.95	50	83.8	82.7	74.0	64.2	63.4	58.2	51.9
10.80	70	84.4	82.9	77.7	65.9	64.4	59.2	54.3
11.10	100	85.4	83.5	77.2	67.4	65.4	61.4	57.2

Table 29. Dispersion of various soloids at different pH values

Added m.e. of alkali to 50 gm. soil	Li		Na		K		NH_4		Ca		Mg	
	pH	Clay .005mm.	pH	Clay	pH	Clay	pH	Clay	pH	Clay	pH	Clay .005mm. per cent
10	6.2	16.1	6.1	9.2	6.0	4.2	6.0	5.3	5.2	5.0	4.9	5.1
20	8.0	32.2	8.0	18.3	8.0	5.6	7.8	7.2	6.0	5.8	6.8	6.2
30	9.3	42.0	9.3	28.2	9.3	5.8	9.2	9.5	7.0	6.6	8.2	7.3
40	10.1	52.7	10.0	40.2	10.2	7.5	9.4	11.8	8.0	6.7	8.7	9.1
50	10.4	56.8	10.3	49.4	10.5	11.8	9.5	14.6	8.6	7.6	8.9	9.7
60	10.6	59.5	10.6	57.5	10.8	13.5	9.4	15.5	8.8	7.9	9.1	10.3
70	10.8	59.6	10.7	59.1	10.9	17.8	9.4	18.0	9.0	7.6	9.2	10.7
80	11.1	60.0	11.1	60.8	11.2	25.7	9.5	20.0	9.0	7.2	9.5	10.8
90	11.2	61.3	11.2	63.1	11.2	27.9	9.5	21.8	9.1	6.0*	9.6	6.5*
100	11.2	61.4	11.2	63.2	11.3	31.0	9.6	23.1	9.2	4.0	9.7	2.0
110	11.2	63.9	11.3	63.9	11.4	30.6	9.6	22.8	9.2	3.2	9.7	1.8
120	11.3	61.8	11.3	67.8	11.4	34.2	9.6	24.5	9.2	3.0	9.7	1.0
130	11.3	61.5	11.3	68.3	11.4	32.8	9.7	26.2	....	....	9.7	....
140	11.3	62.9	11.4	71.6	11.4	23.1*	9.7	26.8	....	....	....	....
150	11.6	64.9	11.5	F	11.7	15.4	9.8	26.8	....	....	....	....

the suspended matter in every case. The results are given in Table 29.

It is also clear that though the pH value of K soil runs parallel to those of Li and Na soils, its dispersion is by no means equal to them and falls more in line with ammonium ions, though the maximum pH value reached with the latter is much lower. The dispersion is the least with divalent ions and so is the maximum pH value.

Complete mechanical analysis of P.C. 13 soil dispersed with different bases was also made. Sixty milliequivalents of alkali were added to 50 grams of the H soil in every case, and suspensions left for 3 weeks, after which they were mechanically analyzed. The results are given in Table 30. It is seen that the effect of different

Table 30. Complete mechanical analysis of a soil dispersed with different bases (after keeping for 3 weeks), 60 m.e. of alkali added to 50 gm. of soil in every case

Base	0.06 mm. (%)	0.04 mm. (%)	0.02 mm. (%)	0.01 mm. (%)	0.008 mm. (%)	0.005 mm. (%)	0.002 mm. (%)
Li	82.9	79.1	76.9	66.4	64.8	60.1	55.3
Na	82.9	79.7	75.4	66.6	64.1	60.7	55.3
K	52.2	43.3	27.8	17.4	17.1	12.4	6.8
NH_4	57.4	47.1	36.7	23.8	21.2	17.0	14.5
Ca	48.4	35.1	25.6	10.2	9.0	8.0	4.8
Mg	55.4	41.9	28.0	14.6	14.0	10.4	6.0

ions on dispersion is similar to that of various pH values; it would seem that clay is uniformly distributed throughout the entire soil, and as dispersion increases each fraction contributes a share of clay proportional to its size and surface.

Effect of Temperature on Dispersion

The effect of temperature on dispersion at different pH values was studied by keeping the H soil with increasing percentages of NaOH in thermos flasks for 24 hours and also by shaking mechanically for the same period. There was a change of temperature of about 5°C during the period the suspension was kept or shaken. The results, given in Table 31, show that an increase in temperature

Table 31. Effect of temperature on dispersion at different pH values

m.e. of NaOH added to 12 gm. of soil	Kept for 24 hours without shaking					Shaken for 24 hours				
	pH	8-12°C	17-22°C	28-33°C	38-44°C	pH	9-14°C	19-25°C	30-35°C	39-49°C
1.5	6.3	9.4	13.4	15.4	17.0	6.2	28.2	29.8	32.8	32.2
3.5	7.0	19.2	21.6	24.0	28.4	7.0	31.6	33.6	36.0	36.6
5.0	9.0	25.6	27.6	29.4	32.4	8.0	34.6	37.0	39.6	39.4
6.5	9.9	27.6	29.8	31.6	36.0	9.2	42.6	46.0	47.6	49.6
9.0	10.5	29.2	33.6	37.0	39.6	10.1	50.2	54.4	55.6	55.8
11.0	10.9	29.6	35.8	40.8	42.8	10.6	55.4	56.4	59.6	60.8
16.5	11.2	37.0	40.8	41.6	50.0	11.1	59.0	58.6	58.4	61.4
25.0	11.6	41.5	45.9	49.6	62.6	11.5	57.9	58.9	58.1	62.1

brings about a higher dispersion at all pH values, the maximum difference being shown at the highest pH value when the suspension was not shaken. The maximum value, however, showed little difference when the suspension was shaken.

The same effect is shown in a more striking manner in Table 32 in which the rate of dispersion of the soil at two temperatures is

recorded. At 35°C the soil is completely dispersed in about 4 hours, whereas at 11 to 12°C it took no less then six days to reach the same state of dispersion.

The enhanced rate of dispersion at higher temperature confirms the view already held that the slow rate of interaction between alkali and soil acidoid is due to the slow rate of diffusion of alkali in minute capillaries. The well known effect of temperature on rate of diffusion agrees with the observation recorded above. We can visualize the mechanism of neutralization of an undispersed soil somewhat as follows: The added alkali immediately attacks the particles nearest to it, which are neutralized up to the limit of the availability of alkali in solution. However, particles inside the aggregate

Table 32. Effect of temperature on rate of dispersion

Time	% of 0.005-mm. particles at pH 11.0	
	35°C	11-12°C
4 hours	64.2	....
8 hours	64.6	26.6
12 hours	65.2	28.8
24 hours	62.3	32.1
48 hours	63.0	39.1
3 days	62.9	....
4 days	61.9	49.3
5 days	62.2	54.8
6 days	61.2	58.2
7 days	61.6	60.0
14 days	62.2	61.7

structure receive a smaller share of the alkali. In the course of time, the overneutralized particles slowly give up their alkali to those that were not easily accessible at first. The pH value gradually goes down as equilibrium is reached; but those particles which had attained a certain level of dispersion corresponding to the amount of alkali added remain dispersed, causing only a feeble dispersion of the others.

Reclamation of Alkaline Soils

The phenomenon of auto-disintegration plays an important part in the production of adverse physical condition in alkaline soils. Such soils pass into suspension on coming into contact with water. The fine clay particles thus separated fill up the interstices and prevent aeration and movement of water. This is one of the main causes of the unfertility of these soils. Since $CaSO_4$ is used for the amelioration of alkaline soils, it is of great practical importance to determine how it affects auto-disintegration in Na soils.

There is another interesting point: all the soils show the minimum dispersion when the concentration of $CaSO_4$ is approximately 0.001N. This is remarkably low, considering that a saturated solution of $CaSO_4$ is approximately 0.04N. These results also indicate that it may be more advantageous to apply $CaSO_4$ in the form of a solution by adding the correct amount to the irrigation water rather than applying it at the rate of so many tons per acre. The problem, however, is complicated by the fact that it is not merely a question of adding a certain minimum concentration of $CaSO_4$, but of maintaining that concentration under field conditions.

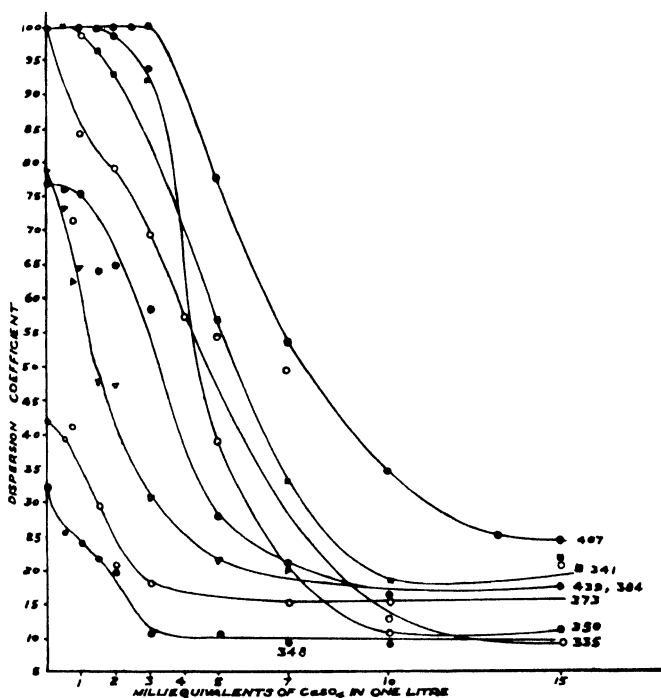



Fig. 38. Effect of $CaSO_4$ on Dispersion Coefficient

Fourteen soils were chosen for this study. These were selected to obtain a wide variation of the degree of alkalization. Ten-gram portions of the soils were auto-disintegrated for 24 hours in a liter of $CaSO_4$ solution of increasing concentration, and the clay determined by the pipette method. The results, expressed in terms of dispersion coefficient, are plotted in Figure 38, only those curves being given which could be accommodated in one diagram. They lead to the conclusion that dispersion is reduced to the minimum at a definite concentration of $CaSO_4$ in solution for each soil. In other words, for the reclamation of alkaline soils, a certain minimum concentration of $CaSO_4$ must be maintained in solution. This can be interpolated from the dispersion-concentration curves, and the

values obtained correlated with the amount of Na saloid in the soil. This will be clear from Figure 39 in which these values are plotted.

Replacement of Calcium by Sodium

Hitherto we have considered the auto-disintegration of Na soils derived from H soils, because the latter offer the starting point for introducing other cations in regulated amounts. Calcium is by far the most important cation in all agricultural soils. We have seen, however, that Ca soils show practically no dispersion by auto-disintegration. It is therefore of interest to know how the dispersion

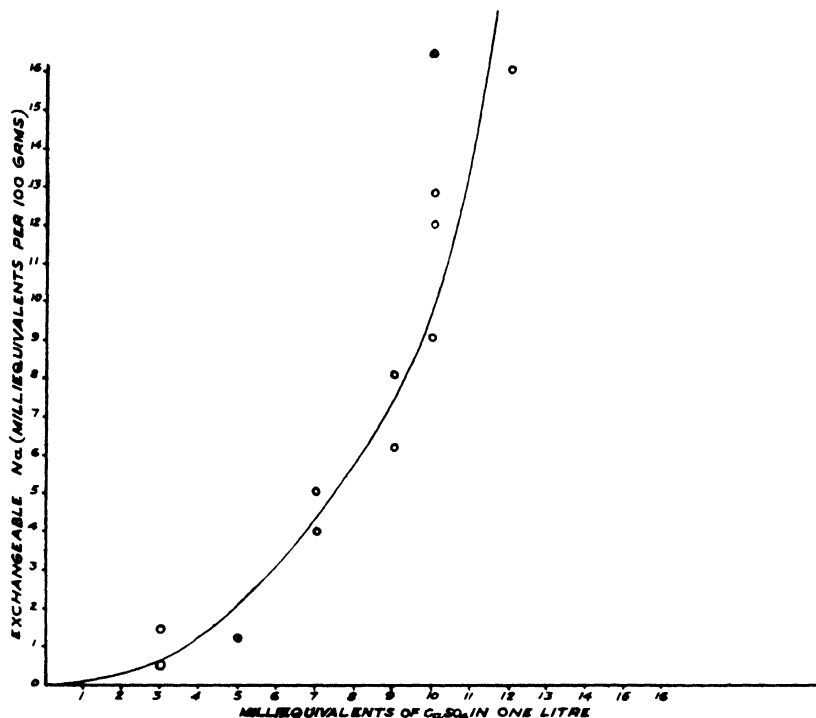



Fig. 39. Relation between Exchangeable Na and Minimum Dispersion Concentration of $CaSO_4$

of a soil will increase with the gradual replacement of Ca by Na. This replacement can be brought about most conveniently by the addition of Na carbonate and Na oxalate to a Ca soil. Increasing percentages of Na_2CO_3 or Na oxalate were added and dispersion studied after 24 hours of auto-disintegration. The results are shown graphically in Figure 40 and 41. The two sets of curves are essentially similar, Na oxalate showing higher dispersion than Na_2CO_3 at every concentration until the maximum value is reached.

Maximum clay was also determined and the results are plotted as dispersion coefficients, i.e., the clay obtained by auto-disintegration expressed as percentage of the maximum clay. It will be seen

that in most cases the maximum value of the clay is obtained by auto-disintegration with Na carbonate or oxalate. In view of the fact that the pH value of the soil cannot be raised to 10.8 with Na carbonate or oxalate, the failure of some soils to give maximum dispersion is easily comprehensible.

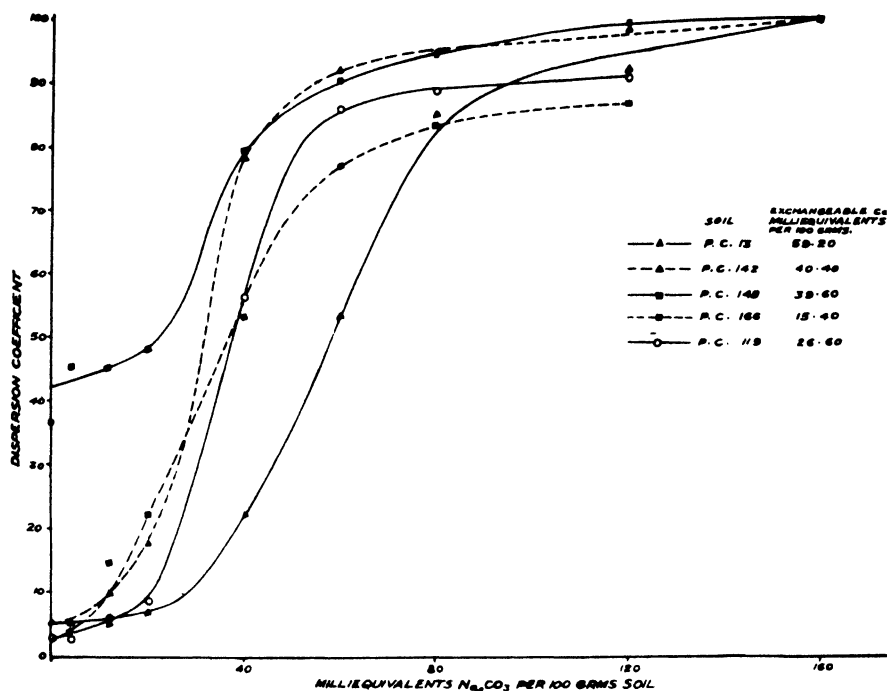



Fig. 40. Auto-Disintegration of Ca Soils with Na_2CO_3

Causes of Dispersion

At this stage it appears pertinent to ask what may be the cause of dispersion and why Na and Li saloids show the highest dispersion? It is true we have the analogy of soluble salts, which show the highest solubility of Na and Li salts and also the greatest ionization. These ions are also supposed to be hydrated and their greater solubility may be due to their ionization or hydration. We can decide this point to some extent in the case of soils. If the ions are hydrated, this hydration must affect the rate of settling of the clay particles. Actually this is not so, for a completely dispersed clay is unaffected by the nature of the cation in it, provided it is not allowed to dry. All the monovalent ions, which should be hydrated, show the same percentage of clay. Hydration, therefore, cannot be a factor in their dispersion or stability.

There is another method of throwing light on this point: clay can be determined at higher temperature and if hydration is playing any

part, there should be a decrease in the clay content due to dehydration. P.C. 13 and P.C. 123 soils were chosen for this experiment as they had the highest base equivalent and therefore would be likely to show the maximum effect of hydration, if any. The soils were brought to a state of maximum dispersion followed by acid treatment. They

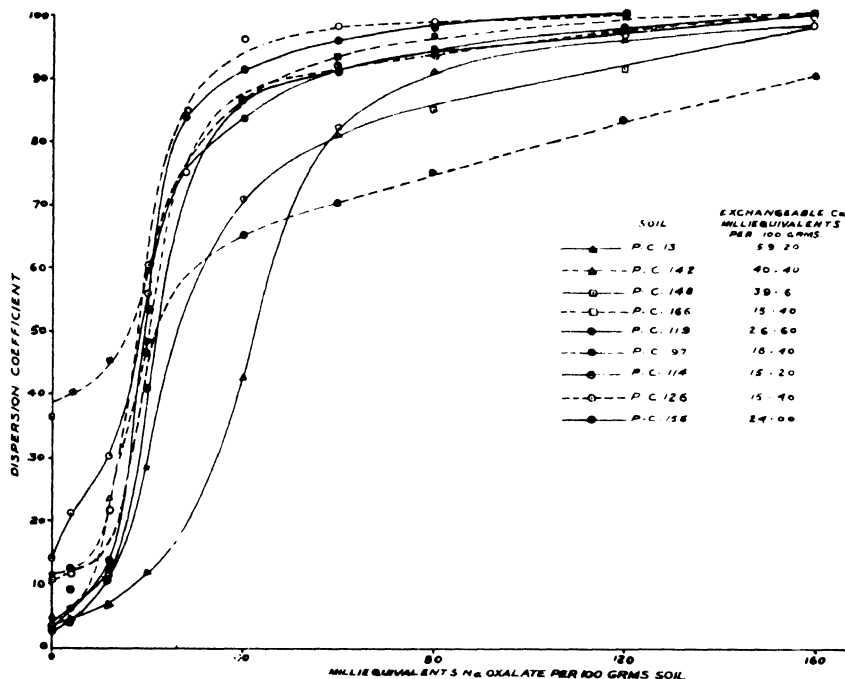



Fig. 41. Auto-Disintegration of Ca Soils with Na Oxalate

were then treated with various hydroxides in equivalent amounts corresponding to the complete neutralization of the acidoid. Clay was determined at three different temperatures, the highest being 64°C in the case of P.C. 13 and 58°C in the case of P.C. 123. The results given in Table 33 leave no doubt that whatever other effect hydration may have, it has no influence on settling.

Since hydration does not seem to play any role in the dispersion of soils, it is probably the higher dissociation of Na and Li salts which causes greater dispersion. We know, for instance, that the conductivity of the Na salt of a weak, feebly ionized acid is appreciable, and very likely the same thing is happening in the case of soils.

We can obtain evidence of the comparative dissociation of the various saloids formed when soil acidoid is neutralized with different bases from: (a) exchange ratios, (b) pH value, (c) conductivity, (d) dispersion, and (e) effect of dilution on dispersion.

Table 33. Effect of temperature on the clay content of soils at maximum dispersion with different ions

Soil P.C. 13 Nature of ion	% clay (0.002 mm.)		
	1°C	25°C	64°C
Ba	55.0	55.7	Flocculates
Ca	52.0	53.9	49.6
Sr	53.7	54.9	54.1
Mg	53.2	54.6	52.1
H	51.2	53.9	50.8
NH_4	50.9	52.8	53.3
K	52.0	53.6	53.5
Na	53.8	56.2	55.6
Li	52.7	56.4	54.2
P.C. 123	1°C	24°C	58°C
Ba	74.9	78.8	73.4
Ca	76.5	78.4	75.1
Sr	76.8	76.2	73.8
Mg	77.8	75.4	74.9
H	75.0	73.0	72.8
NH_4	77.8	77.0	71.2
K	74.6	76.4	73.8
Na	75.3	78.8	74.4
Li	77.1	79.5	74.9

Exchange Ratios

As soil suspensions behave in every way like solutions of weak electrolytes there is no reason why factors like the "solubility product" and pH value, which determine the ionic combination in systems of electrolytes, should not operate in the case of soils. In other words, the formation of that saloid will be favored which is the least ionized. It follows also that those ions which form the least ionized saloid will have the greatest power of replacing other ions. The distinction between a soluble and an insoluble substance is purely one of degree and even the so-called insoluble salts are well known to have a "solubility product", which plays an important part in their precipitation and separation from other salts.

If we add to a Ca soil the Na salt of an anion which can form a Ca salt having a smaller solubility product than the Ca soil, then practically all the Ca in the soil could be precipitated and replaced by Na. This is what happens when Na carbonate or oxalate is added to a Ca soil. The entire phenomenon of base exchange in soils rests on this principle: namely, that if we have a high enough concentration of any salt, then the ionization of the saloid of that cation which is common with the salt will be suppressed so much that we shall have the formation of the major portion of the saloid. For instance,

if we shake a Ca saloid with sufficient amount of normal NaCl, the ionization of the Na saloid will be suppressed so much that it will be rendered less "soluble" than even Ca saloid. However, when equivalent amounts of any two salts are present, the ratio of the two saloids formed will be in proportion to their ionization, i.e., the least ionized is formed to the largest extent. Thus by studying the exchange ratios we can get a fair idea of the ionization of the various saloids.

Exchange ratio may be defined as the ratio of saloids of two cations formed when equivalent amounts are added to a soil at the same time. For instance, if an equivalent amount of KCl is added to a Ca saloid, or $CaCl_2$ to a K saloid, the binary systems being the same in both cases, the final equilibrium will be the same. The

Table 34. Exchange ratios between calcium and other ions

Combination of ions	Exchange ratio
$Ca(OH)_2$-KCl	1.6
KOH-$CaCl_2$	1.5
$Ca(OH)_2$-NH_4Cl	1.8
NH_4OH-$CaCl_2$	1.7
$Ca(OH)_2$-NaCl	4.0
NaOH-$CaCl_2$	4.0
$Ca(OH)_2$-LiCl	4.6
LiOH-$CaCl_2$	4.6
$Ca(OH)_2$-$BaCl_2$	0.8
$Ba(OH)_2$-$CaCl_2$	0.77
$Ca(OH)_2$-$MgCl_2$	1.07

ratio Ca/K in the mixed saloids may be spoken of as the exchange ratio for these particular ions. If all the other ions are compared with Ca taken as unity, we can have a uniform scale of comparison which would give a very good idea of their displacing power.

Since the base taken up by a soil is a continuous function of the pH value, the main difficulty in a comparison of this nature is to fix the reaction of the soil at which the exchange ratio should be determined. In order to gather information on this point the exchange ratio between Ca and Na was determined at different pH values for a number of soils. It was soon discovered, however, that determination of the exchange ratio would be logically sound only in the neighborhood of the neutral point, to avoid complications due to the production of exchange acidity in H soils and the precipitation of Ca in highly alkaline soils. The procedure adopted to determine the exchange ratio of two cations was to add to the hydroxide of the one the chloride of the other in quantities equivalent to the T/2 value of the soil. The exchange ratios for a soil for various ions taking Ca as unity are given in Table 34.

The significance of the values is that an exchange ratio of, for instance, 4 indicates that Ca can displace 4 times (in equivalence) the amount of the other ion from its saloid when the two are present in equivalent amount. In other words, when equivalent amounts of the two ions, one as hydroxide and the other as a neutral salt, are shaken with soil, the Ca saloid formed will be 4 times the Na saloid.

The pH value of a weak acid with a strong base reflects the strength of the base in the extent of hydrolysis, which manifests itself in a higher pH value. Therefore, if equivalent amounts of various bases are added to an acid or acidoid, the resulting pH value will be higher the stronger the base. This higher pH value will indicate a greater dissociation of the saloid. The results in Table 35 show that for a given amount of alkali added, the pH value is

Table 35. Relation between pH value, equivalent solubility, exchange ratio, and dispersion factor

Saloids	pH	Eq. solubility	D.F.	Exchange ratio
Ba	5.57	0.009	7.8	0.78
Ca	6.18	.017	6.7	1.0
Mg	6.23	.014	13.8	1.07
NH_4	8.20	.023	8.5	1.75
K	6.50	.046	24.0	1.65
Na	8.83	.038	63.2	4.0
Li	8.15	.041	63.9	4.6

least in the case of Ba and highest for Na. Conductivity of the suspensions, the pH values of which are given in Table 35, were determined and are represented as concentrations of NaCl, which has the same specific conductivity as the suspension. This method of presentation gives a direct comparison of the different saloids in an easily comprehensible manner.

In Table 35 pH, equivalent solubility, and exchange ratios are given as well as the dispersion factor (D.F.); clay percentage obtained by simple shaking. It will be seen that there is a striking parallelism between the various factors which emphasizes their relationship and interdependence.

If dispersion is due to dissociation of the saloid, then dilution of the suspension, which by analogy to soluble salts would increase dissociation, should have the effect of increasing the dispersion. This is actually the case, as was shown by the following experiment: 12-gram portions of a highly clayey H soil were dispersed at different pH values by keeping them in contact with 200, 400, 600, 800 and 1000 cc of water for 10 days, with no mechanical shaking. After that the volume was made up to 1,200 cc in every case to give 1 per cent suspension. The results are recorded in Table 36.

The effect of dilution is not apparent up to pH 9.82, but at higher pH values the higher dilutions give greater dispersion. The soil used for this experiment (P.C. 123) was extremely sensitive to pH changes as regards dispersion and therefore particularly suited for the purpose. After the addition of alkali to the 1% suspension, samples were kept for ten days, with no shaking. These results again point to the analogy between solutions of weak electrolytes and clay suspensions. The increase in dispersion on dilution fits in well with the increase in activity of electrolytes on dilution.

Table 36. Effect of dilution on dispersion at different pH values

cc. of N NaOH added to 12 gm. of soil	pH taken after 10 days	Volume (cc.)	0.06mm. (%)	0.02mm. (%)	0.01mm. (%)	0.005mm. (%)	0.002mm. (%)
		200	75.8	51.2	38.8	35.2	33.0
		400	77.0	54.8	41.6	36.4	35.6
3	9.20	600	74.4	51.6	39.2	34.8	35.3
		800	76.6	49.0	39.8	34.8	33.0
		1000	76.6	48.8	38.9	34.6	33.2
		200	83.3	58.4	48.8	45.6	45.5
		400	82.4	60.8	52.0	47.6	45.3
5	9.82	600	83.4	59.8	51.0	47.1	46.4
		800	82.9	56.8	48.4	45.0	44.8
		1000	.....	.....	.....	.....	.....
		200	84.6	66.2	62.2	56.6	56.3
		400	85.1	65.6	64.3	58.2	57.9
8	10.36	600	87.2	74.6	70.6	67.4	65.9
		800	88.4	75.4	71.9	67.9	67.7
		1000	89.0	76.6	72.4	68.4	68.2
		200	87.9	74.8	68.8	62.5	61.7
		400	89.8	79.2	74.4	72.4	71.0
16	11.40	600	92.0	83.8	82.0	80.0	78.8
		800	92.9	83.0	81.7	79.4	78.8
		1000	93.6	84.8	83.0	81.9	80.4

Flocculation

If dispersion is due to dissociation of the saloid, coagulation or flocculation must be due to the suppression of this ionization by a common ion effect. Flocculation of H clay by hydroxides of Ca, Sr, and Ba was studied in the first instance. The concentration of the suspension was varied from 0.0826 to 3.246%, but the total amount of suspended clay in a given suspension was kept the same in all cases. The results, plotted in Figure 42, bring out the interesting fact that with increased dilution larger amounts of the various hydroxides are required to bring about flocculation, and also that equivalent amounts of the various hydroxides are required to flocculate the suspension. The results are as expected; for instance, since increased dilution would lead to increased dissociation, larger proportions of the common ion would be required to suppress the

ionization to the point of coagulation. Again, to produce the same coagulation concentration of the various ions, larger percentages will be required when the volume of the suspension is greater (i.e., in dilute suspension, since the amount of clay in every case was kept the same).

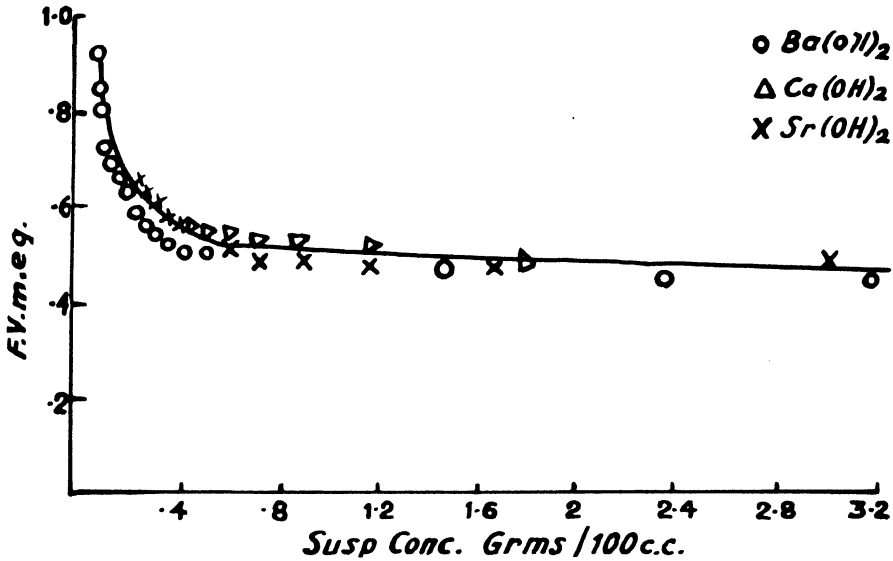



Fig. 42. Effect of Concentration of Suspension on F.V. for Hydroxides of Ca, Sr, and Ba

Table 37. Base neutralizing power of soils and F.V. for $Ba(OH)_2$

Soil No.	T/2 value m.e. per 5 gm.	F.V. m.e. per 5 gm.
1	1.215	1.25
2	0.825	0.95
3	1.080	1.03
4	1.485	1.07
5	1.395	1.65
6	0.795	0.76
7	1.460	1.34
8	1.305	1.34

From these results, one would expect the flocculation to occur on the addition of an alkali to a H soil suspension only after the saloid formation has taken place, and it is the amount of the alkali above the equivalent point that would subsequently suppress the ionization of the saloid. This is well brought out in Table 37, in which the flocculation values for $Ba(OH)_2$ for a number of H soils along with their T/2 values are given.

If on the other hand we have a highly ionized Na saloid, a much larger amount of $Ba(OH)_2$ will be required to suppress its ionization, and the gradual addition of NaOH to a H soil will lead to a gradual increase in the F.V. value by $Ba(OH)_2$. This will be clear from Figure 43 in which the F.V. value for $Ba(OH)_2$ is plotted against the percentage neutralization of the soil with NaOH, taking the T/2 value as 100% **neutralization.**

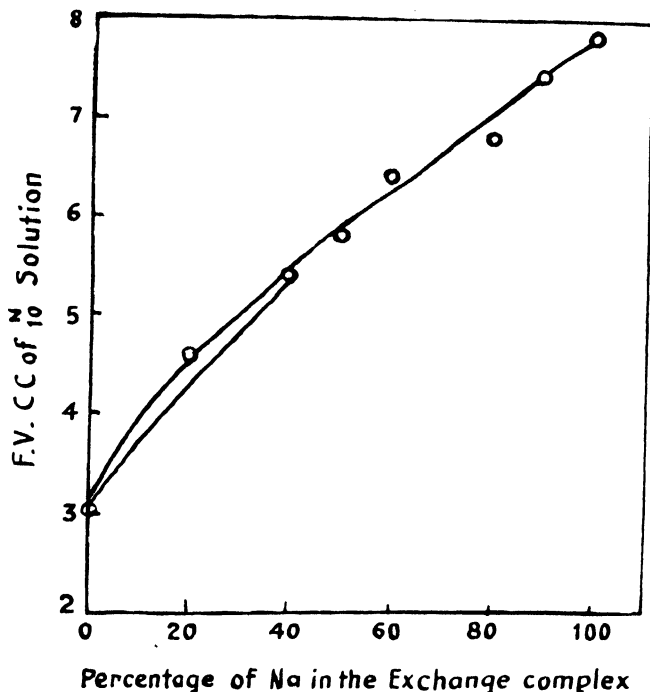



Fig. 43. Flocculation of Soils Containing Increasing Amounts of Na Saloid with $Ba(OH)_2$

Flocculation by acids is complicated by side reactions. If it is a H soil, some aluminum and iron are sure to be brought into solution. If it is a saloid, the acid must react with the cation and bring into solution a corresponding amount of the salt. Unless these side reactions could be accounted for, no useful purpose would be served by this study.

Flocculation by neutral salts is also subject to the exchange of one ion for the other, but such a study would be useful especially in the Ca-Na saloids, because flocculation and dispersion play an important part in natural soils and these are the two cations that are chiefly concerned.

Varying concentrations of clay suspensions were prepared by diluting the H clays to various extents; the minimum concentration of $CaCl_2$ required to produce flocculation was determined in each case. The values are given in Table 38.

The results show that beyond a certain concentration, the flocculation value becomes independent of the concentration in all the H clays studied. The respective pH values of the H clays were then raised by the addition of NaOH and the flocculation values for $CaCl_2$ determined. The results are included in Table 1, and are similar to those recorded in the case of H clays, except that very much

Table 38. Effect of concentration of clay suspension on flocculation values

Concentration of suspension (%)	F.V. milliequivalents per liter					
	P.C. 123		P.C. 172		P.C. 180	
	H	Na (pH 8.7)	H	Na (pH 8.4)	H	Na (pH 9.4)
0.25	0.4	3.0	0.4	2.8	0.8	3.0
0.50	0.7	5.8	0.8	6.0	0.8	5.8
1.00	1.2	10.4	1.4	9.0	1.5	9.6
2.00	1.8	11.0	1.8	10.0	2.2	10.4
2.50	2.0	11.0	2.0	10.4	2.4	10.6

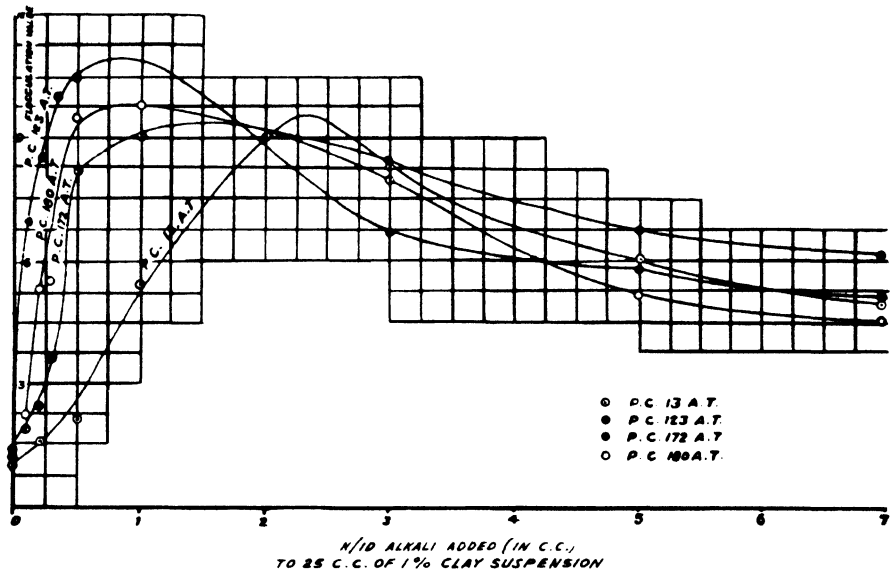



Fig. 44. Effect of Adding Increasing Amounts of NaOH to H Clays on the Flocculation Value of $CaCl_2$

larger amounts of $CaCl_2$ are required to flocculate the same concentration of clay at higher pH value. This led to the study of the variation produced in the coagulation values when the H soil is gradually neutralized with an alkali. With this end in view, increasing percentages of NaOH were added to the H clays and the suspensions shaken for 48 hours, after which they were diluted to give 1% concentration. The coagulation values for $CaCl_2$ were determined in each case. The results are plotted in Figure 44.

The point where the maximum coagulation value occurs is different in different clays. From the titration curves of these soils, the neutralization point, i.e. (T/2 value), is determined. It is found that the neutralization point and the point where the flocculation value is the maximum coincide. This will be clear from Table 39.

Table 39. Relation between neutralization and maximum F.V. values

Soil No. P.C.	Max. F.V. value	T/2 value	pH at max. F.V.	pH at neutralization
13	2.35	2.40	9.8	10.0
123	0.95	1.10	10.3	10.3
172	1.20	1.20	10.3	10.1
180	1.00	1.04	9.8	9.7

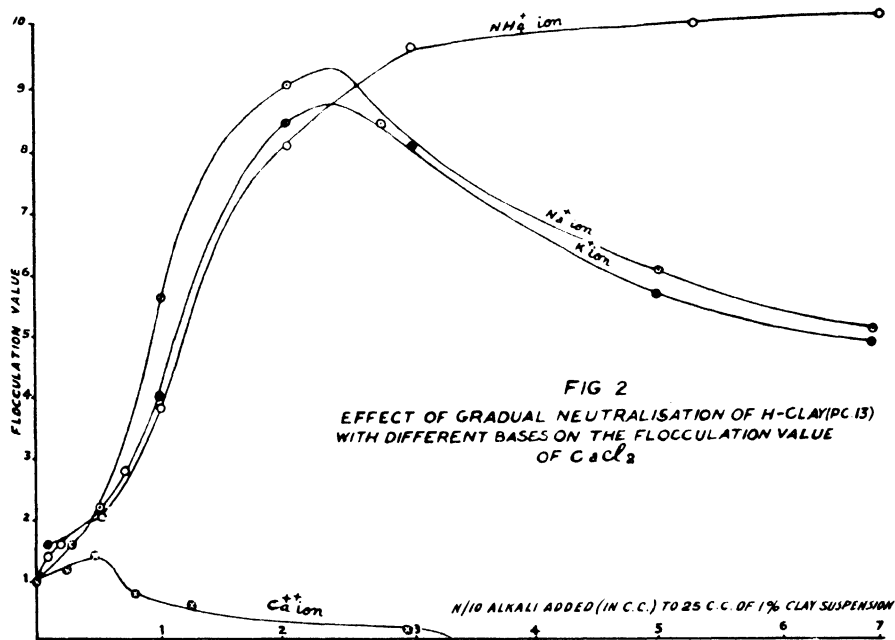



Fig. 45. Effect of Gradual Neutralization of H Clay (P.C. 13) with Different Bases on the Flocculation Value of $CaCl_2$

It appears from the foregoing that when the base-neutralizing power of a H clay is fully satisfied, further addition of alkali flocculates it, instead of peptizing it. This merely shows that ionization of the Na saloid is maximum at the neutral point. As more alkali is added the effect of the rising concentration of the common ion is to reduce ionization and the F.V. decreases beyond this point.

Similar observations were made by gradually neutralizing P.C. 13 clay with KOH, NH_4OH and $Ca(OH)_2$ and determining the flocculation values as before. Results are plotted in Figure 45. The curve

obtained by using NaOH is also included in this figure for the sake of easy comparison. The effect of KOH is analogous to that of NaOH. With ammonia, however, no reversal of the curve takes place, because a weak alkali like ammonia would give very few common ions to reduce the already feeble ionization of ammonium saloid.

With $Ca(OH)_2$ the flocculation value increases but little in the beginning and soon after begins to fall. This is due to the very low ionization of Ca saloid.

CHAPTER XVII

ELECTRODIALYSIS OF SALOIDS IN THE SOIL

The method of separating crystalloids from colloids by diffusion, accelerated by an electric current, is known as electrodialysis. The term as applied to soils is a misnomer. In reality it is a simple case of electrolysis in which a saloid is split up into its component parts, namely, base and acidoid. As such it is no different from similar electrolysis of soluble electrolytes.

The retention of the term "electrodialysis" in this discussion has the backing of extensive usage in soil literature and it is feared that a change might cause confusion. It is emphasized, however, that a recognition of the essential similarity between electrodialysis and electrolysis is essential for retaining a proper perspective of the phenomena to be discussed.

The application of electrodialysis to soils is chiefly due to Mattson, who worked extensively on electrodialyzed clays. An electrodialyzed clay is a H clay or an acidoid, the properties of which we have already discussed. The Mattson cell consists of three compartments separated by a semi-permeable membrane. This was modified by Bradfield, who introduced a two-compartment cell consisting of an Alundum extraction thimble, supported by a nickel cathode suspended in a specially constructed glass cell with a side arm. Several other workers introduced ingenious modifications when this subject was the fashion of the day.

Actually an electrodialyzed soil could be produced much more easily and thoroughly by a simple treatment with a dilute acid; therefore, as a laboratory aid in routine analysis its use is limited and has rightly gone out of fashion. But as an aid to the fundamental elucidation of the behavior of saloids it has proved very valuable.

One of the simplest and most easily constructed pieces of apparatus is shown in Figure 46. It consists of an ordinary glass funnel and a perforated copper cone, which serves as the cathode. The anode is a platinum gauze (a platinum wire shaped into a coil serves equally well) attached to a glass tube, held in a wooden cover, which also holds a V-shaped glass tube (not shown in the diagram) for circulating water. A filter paper is fitted into the copper cone as in ordinary filtration, and after the cone is filled with soil suspension the electrodes are connected with the electric main through a rheostat.

Instead of a stout perforated cone, nickel or copper gauze shaped like a cone can be used. A stout filter paper is preferable, but almost any brand can be used. The amount of soil that can be treated

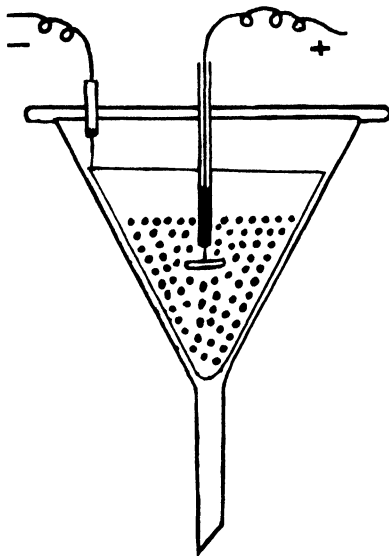



Fig. 46. Diagram of Electrofiltration Apparatus

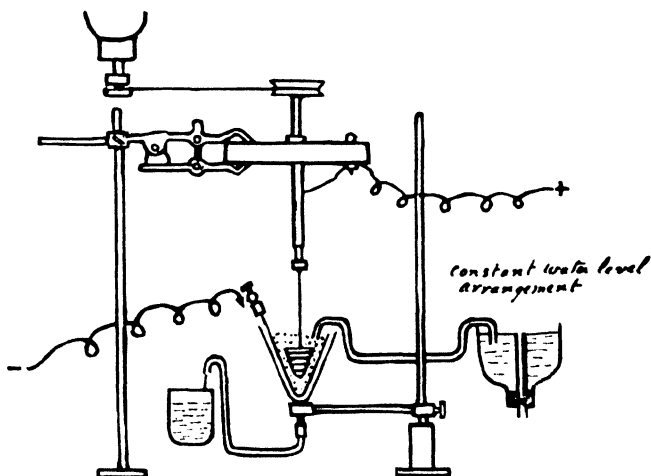



Fig. 47. Diagram of Apparatus for the Electrodialysis of Soils by the Rotating Electrode

at a time depends on the size of the apparatus, for which there is no limit. Sometimes the filtration is too rapid, and a stopcock attached to the funnel is required to regulate the flow. As opposed to electrodialysis this apparatus could be more appropriately described

as performing electrofiltration, but essentially its function is the electrolysis of soil saloids.

This simple apparatus is capable of several variations. A Buchner funnel could be substituted for an ordinary funnel, its porcelain disc replaced by a metallic one which serves as the cathode. Its adaptation for a rotating electrode is shown in Figure 47. The use of the rotating electrode in ordinary electroanalysis is well known. The advantage claimed for this type of electrode is that by causing it to rotate at a high speed, greater current intensity and higher voltage can be applied, giving more rapid separation of the respective metals. In this case the rotating anode is cone-shaped and is made from a perforated sheet or gauze of gold or platinum. It is rotated at about 200 to 300 revolutions per minute. Currents as high as 0.5 ampere can be passed from the mains with a suitable sliding resistance. Currents higher than 0.5 ampere result in too much heating.

A comparison between the rotating anode and a stationary one under identical conditions led to the following conclusions:

(1) Electrodialysis, as revealed by the percentage recovery of bases, is quicker with the rotating electrode than with the stationary one.

(2) Different bases take varying lengths of time for displacement by the same current density. The order of their ease of displacement is Na > K > Ca > Mg.

(3) There is very slight recovery of Mg, and it is doubtful if the total content could be recovered by electrodialysis within a reasonable time.

(4) The volume of the electrodialyzate is slightly greater and the maximum temperature of the anode chamber slightly higher for the stationary anode than for the rotating one.

(5) Currents as high as 0.5 ampere can be passed using the rotating electrode, without too much heating. With this current, the splitting up of the saloid and recovery of the bases is complete in less than an hour.

(6) The advantages of a rotating electrode are greatly minimized when the anode is large.

It is worthy of note that a large proportion of the alkali in the dialyzate may be converted into carbonate, or even bicarbonate. This tendency is greater after electrodialysis has gone on for some time. Another point to be remembered is that the water used for electrodialysis should be tested for alkalinity. If the water is even slightly alkaline, appreciable error in the results can be introduced especially if the volume of the electrodialyzate is large, as frequently happens, and the total bases are not high.

Electrodialysis has a limited value as a means of determining cations in soils, especially in the case of Mg, but the rotating electrode has proved extremely useful in throwing light on a number of phenomena bearing on the mutual relationships between saloids. These are dealt with below.

Speed of Electrodialysis of Different Cations

It is well known that the rate of electrodialysis is different for different cations in soils. If, however, Faraday's law is applicable, the masses that separate should be proportionate to the combining weights of the ions. In other words, the quantities, if reckoned in terms of milliequivalents, should be the same whatever the nature of the cation in the soil. This is actually not the case; for instance, divalent ions are separated more slowly than monovalent ions, and there are differences among ions of the same valency. These differences may be due to either of the following causes:

(1) The rate of electrodialysis may be governed by the state of aggregation of the soil particles. The greater the dispersion of the soil, the greater the rate of electrodialysis.

(2) The experimental conditions in an electrodialysis cell may be such that the base, once separated, can recombine unless removed instantly. The rate of removal, however, may be governed by the dissociation, since current can be carried only by free ions.

(1) State of Aggregation. It has been shown that the state of aggregation of soil particles is governed by the nature of the cation in the saloid, sodium and lithium soils being completely dispersed and other ions imparting a crumb structure of varying degrees. It has also been shown that a fully dispersed soil remains as such irrespective of the changes produced in the nature of the cations, provided it is kept in water and not allowed to dry. Thus a Na soil which is completely dispersed can be converted into a H soil by treatment with 0.05N HCl, and will remain fully dispersed in the wet condition. This H soil can be shaken with different alkalies to produce corresponding saloids, and in all cases the maximum dispersion will persist. This fact affords a simple method of varying the state of aggregation of soil without changing its cations, and vice versa. The effect of state of aggregation, therefore, can be tested.

Electrodialysis was conducted in the cell with a rotating anode. Current was maintained exactly at 0.1 ampere with the help of a sensitive ammeter and sliding resistance. The following single-base soils were prepared from a black cotton soil of high base equivalent:

(a) H soil neutralized with equivalent amounts of different bases and kept wet.

(b) Same as (a), except that soils were dried after treatment with bases.

(c) H soil converted into Na soil, then again into H soil, the last neutralized with different bases and kept wet.

(d) Same as (c), except that soils were dried after treatment with bases (dispersion varying according to the nature of the cation).

A 5-gram portion of each soil was electrodialyzed for 5 hours. Hourly estimates of the alkali removed and the volume of the dialyzate were made and everything else likely to influence the rate of electrodialysis was kept constant.

Table 40. Electrodialysis of single-base soils

5-gm. portions of soil containing 25 cc. of 0.1 N base; current passed = 0.1 ampere

	Calcium soil		Magnesium soil		Potassium soil		Sodium soil		Ammonium soil		Barium soil		Lithium soil		Strontium soil	
	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate	Recovery of base, 0.1 N solution	Volume of electrodialyzate
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
(*A*) *Soils*																
1st hour	8.30	780	3.52	806	12.19	704	19.29	577	9.73	1,270	8.50	1,366	16.85	639	7.69	1,188
2nd hour	3.53	572	1.09	572	3.12	546	3.66	343	2.70	1,018	3.15	1,117	2.60	420	2.80	920
3rd hour	2.50	626	0.95	480	2.80	450	0.84	300	1.05	800	1.70	1,150	1.50	454	2.40	1,050
4th hour	2.21	611	0.87	450	2.47	566	0.63	318	0.95	690	1.70	1,550	0.85	378	1.50	1,060
5th hour	1.84	584	0.59	384	1.99	618	0.87	380	0.70	658	1.30	1,610	0.70	415	1.80	1,185
Total	18.38	3,173	7.02	2,692	22.57	2,884	25.29	1,918	15.13	4,436	16.35	6,793	22.50	2,306	16.19	5,403
(*B*) *Soils*																
1st hour	9.14	698	2.95	615	13.54	683	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
2nd hour	3.60	637	1.58	633	3.67	431	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
3rd hour	2.40	489	1.10	518	2.20	334	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
4th hour	2.09	494	1.12	644	1.68	694	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
5th hour	1.73	511	0.71	590	1.53	532	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Total	18.96	2,829	7.46	3,000	22.62	2,674	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
(*C*) *Soils*																
1st hour	10.71	350	4.53	545	17.05	321	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
2nd hour	3.06	250	1.17	436	4.05	202	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
3rd hour	1.97	308	0.86	374	1.90	187	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
4th hour	1.44	289	0.71	328	0.75	181	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
5th hour	1.29	278	0.62	306	0.28	195										
Total	18.47	1,475	7.89	1,989	24.03	1,086	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
(*D*) *Soils*																
1st hour	8.24	798	3.98	600	11.15	590	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
2nd hour	3.63	480	1.59	505	4.81	245	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
3rd hour	3.14	416	1.13	444	3.20	235	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
4th hour	2.89	399	0.95	506	2.66	328	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
5th hour	2.41	371	0.87	525	1.39	363	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Total	20.31	2,464	8.52	2,580	23.21	1,761	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

The results given in Table 40 show that in every case the differences in the rate of electrodialysis due to the nature of the cation are maintained. Such differences, therefore, are definitely not due to the state of aggregation of the soil, however, this is reflected in the volume of the dialyzate obtained. In spite of the large differences in the amount of the dialyzate, the quantity of base recovered is unaffected. This fact is rather important, as it leads to the conclusion that no advantage, as regards the rate of removal of exchangeable bases, could be gained by increasing the rate of filtration in electrodialysis. In fact, it would be better to reduce the rate of filtration in order to obtain a more concentrated solution of the base removed and to avoid analytical errors that might arise in examining large volumes of solution.

The experiment was repeated with an artificial permutite used for water softening. Permutites are supposed to possess an open structure; therefore, the question of state of aggregation does not arise. The results given in Table 41 show that the differences due to the

Table 41. Electrodialysis of permutites

Time	Sodium permutite		Calcium permutite		Magnesium permutite	
	Recovery of base 0.1N solution	Vol. of electro-dialyzate	Recovery of base 0.1N solution	Vol. of electro-dialyzate	Recovery of base 0.1N solution	Vol. of electro-dialyzate
	cc.	cc.	cc.	cc.	cc.	cc.
1st hour	26.84	598	14.68	1,658	11.15	1,331
2nd hour	20.43	1,259	10.52	1,452	9.65	1,453
3rd hour	12.69	868	9.50	1,340	6.35	1,250
4th hour	13.63	854	5.00	1,645	4.45	1,230
5th hour	12.85	770	4.55	1,690	3.35	1,340
Total	86.45	4,349	44.25	7,785	35.95	6,604

nature of the cation are maintained. The permutite used was in the powdered state. It was leached with $CaCl_2$ and $MgCl_2$, followed by leaching with water to introduce the corresponding ions. It is interesting that the rate of filtration in Na permutite is less than that of Ca or Mg permutite, though the state of aggregation must be supposed to be the same. It may be that Na renders the surface of the particles gelatinous, thus causing greater resistance to the passage of water.

(2) Ionic Activity. We have seen that exchange ratios, conductivity and dispersion all point to the fact that monovalent cations are more highly dissociated than divalent ones, and that the monovalent ions Na and Li far exceed others in the degree of dissociation. It is probable, therefore, that the varying rate of electrodialysis is accounted for by the greater dissociation of Na ions, which leads to a greater conduction of electric current, which may be partly dissipated as heat in other cases. This view is also confirmed by the fact that the rate of recovery of a base decreases as the electrodialysis proceeds, and the soil reaction plays an important part in controlling the speed of electrodialysis.

At this stage an interesting possibility presented itself, i.e., separating Ca and Na from a soil containing both, by differential electrodialysis. Soils of varying pH value and degree of alkalization were prepared from the H soil by neutralization with appropriate amounts of various alkalies or mixtures of NaOH and $Ca(OH)_2$. In preparing soils at different pH values, the amount of alkali was kept constant, the amount of soil being varied. Therefore in any one experiment, though the quantity of soil varied, the amount of Na ion was the same. Current was kept at 0.1 ampere throughout the experiment and the alkali displaced was titrated every half hour. The results are graphically represented in Figure 48. The total

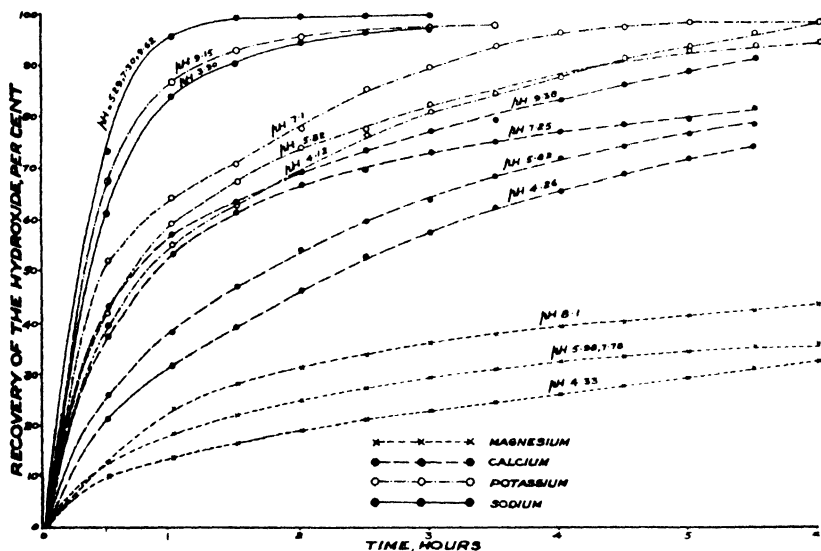



Fig. 48. Effect of pH on the Rate of Recovery of Bases by Electrodialysis

alkali recovered is plotted against successive time intervals in every case. It is seen that the rate of electrodialysis increases with the pH value. This increase in rate, however, is generally confined to the first half hour, after which the various curves show virtually the same relative shift at different time intervals. This is easily understood when it is remembered that the pH value decreases as electrodialysis proceeds, so that the rate of recovery tends to equalize in time.

Separation of metals by electrolysis using the principle of graded potential is well known. An application of the same principle to the quantitative separation of cations in soil saloids is rather limited because the low voltages required for such separation are not possible in the case of soils on account of the extremely low conductivity of soil suspensions. There is, however, the possibility that at low current densities a separation of the monovalent and divalent bases might be effected. It was felt that even if the separation were not complete, a knowledge of the magnitude of the dif-

ferences would be of great interest in dealing with soils having varying ratios of saloids of Na/Ca. For instance, the electrodialysis of such soils might throw light on the availability of the Ca in them.

As a preliminary to this study, the rate of electrodialysis of a Na soil was determined by the use of low currents. It was found that 66 to 70% of the total Na could be removed in 19 hours with a current of 0.005 ampere. The use of still lower currents was not feasible. Since electrodialysis at low current densities is likely to spread over a long period, involving a large volume of the electrodialyzate and necessitating several titrations, the alternative method of estimating Na gravimetrically was also considered. A comparison with the values obtained by simple titration as hydroxide showed

Table 42. Recovery of bases by electrodialysis of (Na + Ca)-soils at different degrees of alkalization, at pH 7, and with current density of 0.005 ampere

DEGREE OF ALKALIZATION... *per cent*	15.40		23.07		30.77		38.46		53.84		69.23		84.61	
Time intervals	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca
hours	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
½	2.19	1.20	1.53	0.70	2.08	0.80	1.16	0.60	2.72	0.40	1.98	0.60	3.01	....
1	0.44	1.10	1.79	0.90	2.31	0.70	1.71	0.60	2.19	0.60	2.10	0.40	3.21	....
1½	....	1.10	....	1.10	1.12	0.80	1.20	0.80	2.52	0.60	2.27	0.30	3.16	0.20
2	....	1.00	....	1.20	0.20	0.90	1.76	0.60	0.88	0.50	1.60	0.70	1.90	0.20
2½	....	1.00	....	1.00	0.18	1.00	0.65	0.60	1.12	0.30	1.51	0.40	2.05	0.40
3	....	0.70	....	0.80	....	1.20	1.05	0.70	0.34	0.60	1.30	0.50	1.41	0.20
3½	....	0.80	....	1.00	....	1.30	0.30	0.90	0.21	0.50	0.85	0.40	2.12	0.30
4	....	0.90	....	0.90	....	1.00	....	1.10	....	0.70	0.65	0.20	2.19	0.10
4½	....	0.90	....	0.60	....	0.80	....	1.00	....	0.40	0.78	0.10	2.20	0.20
5	....	0.80	....	0.80	....	0.80	....	0.90	....	0.70	0.40	0.40	1.78	0.30
5½	....	0.70	....	0.90	....	0.60	....	1.00	....	0.60	0.18	0.80	0.80	0.50
Total........	2.63	10.20	3.32	9.90	5.89	9.90	7.83	8.80	9.98	5.90	13.62	4.80	23.83	2.40

that the gravimetric method gave essentially similar results, and as the soils contained no bases other than those under consideration, simple titration of the electrodialyzate furnished all the information required in this connection.

Two series of soils, of varying degrees of alkalization, one at pH 7 and the other at pH 9, were prepared for this study. Current was maintained at 0.005 ampere in every case throughout the experiment, which lasted for 33 hours. In the two series, 52 and 78 m.e. of total alkali per 100 grams of soil were used to obtain soils at pH 7 and pH 9, respectively. These quantities were determined from the titration curves of the soils. The final pH values differed slightly from 7 and 9, but the variations were not considered significant for the purpose of this experiment. The results are given in Tables 42 and 43. It will be seen that as the degree of alkalization increases, the amount of Na in the electrodialyzate increases, and the amount of Ca decreases.

Table 43. Recovery of bases by electrodialysis of (Na + Ca)-soils at different degrees of alkalization, at pH 9, and with current density of 0.005 ampere

DEGREE OF ALKALIZATION.... *per cent*	15.40		30.07		53.84		69.23		84.61	
Time intervals	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca
hours										
½	2.89	0.40	2.70	0.30	1.90	1.80	1.69	0.90	1.70	0.25
1	1.89	0.50	2.30	0.50	2.46	1.14	2.03	0.50	2.36	0.25
1½	....	1.20	2.25	0.40	1.92	1.15	2.10	1.00	2.53	0.55
2	....	1.20	1.60	0.50	2.20	0.85	2.15	0.50	2.85	0.85
2½	....	1.20	1.40	0.80	1.75	0.80	1.80	1.10	1.90	0.60
3	....	1.20	0.80	1.60	1.52	1.00	1.65	0.85	2.10	0.20
3½	....	0.90	0.75	1.00	1.55	0.70	1.53	1.00	2.00	0.25
4	....	0.90	0.36	1.20	1.60	0.70	1.93	0.60	2.20	0.25
4½	....	1.00	0.25	1.20	1.50	0.80	1.85	0.50	2.00	0.25
5	....	1.20	0.35	1.00	1.17	0.75	1.98	0.30	1.60	0.30
5½	....	1.10	0.20	1.20	1.50	0.50	1.72	0.30	2.10	0.10
Total.........	4.78	10.80	12.96	9.70	19.07	10.19	20.43	7.55	23.34	3.85

The practical significance of these values will be clear from Figure 49, in which the Ca/Na ratio in the entire electrodialyzate is plotted against degree of alkalization. The two curves (for pH 7 and 9) are essentially similar, but at the higher pH value the toxic ratio is probably reached at a lower degree of alkalization than at the lower pH value.

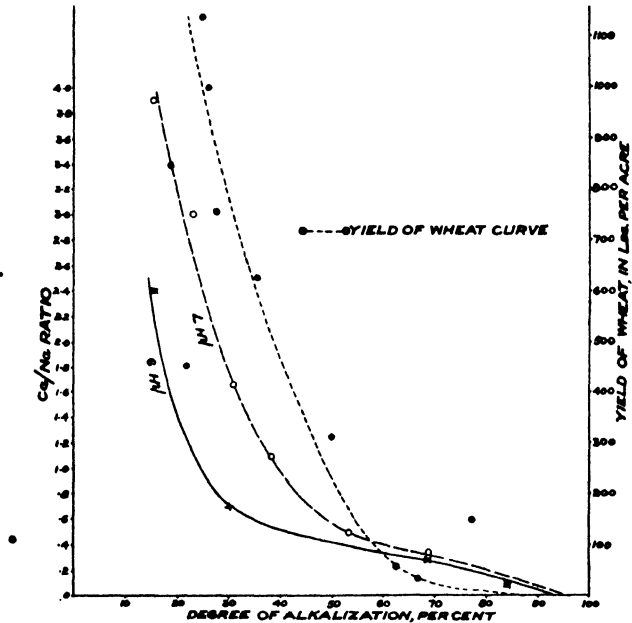



Fig. 49. Relation between Degree of Alkalization and Ca/Na Ratio in the Electrodialyzate and Yield of Wheat

How the deficiency of Ca in soils of high alkalinity, which is reflected in the low Ca/Na ratio in the electrodialyzate, may affect the crop yield is brought out by the curve showing the relation between degree of alkalization and yield of wheat. The observations on yield trials refer to a reclamation farm (Montgomery) having a soil quite different from the one used for electrodialysis (see page 84). The striking similarity of the curves emphasizes the fact that the fundamental cause of infertility of alkaline soils lies in the deficiency of available Ca. It is not unlikely that electrodialysis at low current densities may furnish a useful method of finding the relative availability of different ions, especially in alkaline soils in which deficiency of Ca is an important limiting factor in crop yield. Electrodialysis may be regarded as a diffusion of ions produced by hydrolysis speeded up by electric current. The smaller the current, the nearer the process will approach ordinary diffusion and hence natural conditions.

In the course of this investigation a question of considerable interest arose with regard to the relation between monovalent and divalent bases in the mixture of saloids. If an ordinary soluble acid is partly neutralized with $Ca(OH)_2$ and partly with NaOH, the resulting mixture is exactly the same, whether the one or the other alkali is used first for neutralization. It was of interest to know whether soil acidoid would behave in a similar manner. In a heterogeneous mass like the soil, it would appear at first sight not unreasonable to suppose that the base added first might be the last to come out in the electrodialyzate. On the other hand, if the cations in the soil are mobile, the soil would behave like any ordinary buffer mixture and there would be no distinction, regardless of which alkali was added first. The speed of electrodialysis of a (Ca and Na) soil seemed to offer a promising means of throwing light on this question.

An H soil was partly neutralized with NaOH and shaken for 24 hours. An equivalent amount of $Ca(OH)_2$ or $Mg(OH)_2$ was then added, followed by shaking for 24 hours. Another set of soils, in which the order of addition of hydroxides was reversed, was similarly prepared. The final pH value of the soil was approximately 6.70 in each case. The soils were then electrodialyzed by means of a current of 0.1 ampere. The results showed virtually no difference in the rate of electrodialysis for Na, Ca and Mg in the two sets of experiments. The cations in saloids, therefore, exist in dynamic equilibrium, and the soil buffer behaves in this respect like an ordinary soluble buffer mixture.

In most work on electrodialysis, no notice is taken of the temperature except that too high a temperature is avoided because of the possible side effects. In studying the effect of various factors on the rate of electrodialysis, it is necessary to know the exact part played by temperature. Single-base soils were electrodialyzed for 2 hours at different temperatures, a current of 0.1 ampere being

used. The results, plotted in Figure 50, show that there is perhaps an optimum temperature, somewhere about 30°C, at which the rate of electrodialysis is maximum. This maximum is most prominent in Ca soils. It is difficult to find any valid cause for the maxima especially as the magnitude of the difference follows no definite order, though the convexity occurs at virtually the same temperature in all cases. The results, however, are so regular that any possibility of side effects even at high temperature seems to be ruled out. It is clear from these results that the effect of temperature on the rate of electrodialysis on the whole is so slight that no control of this factor appears necessary.

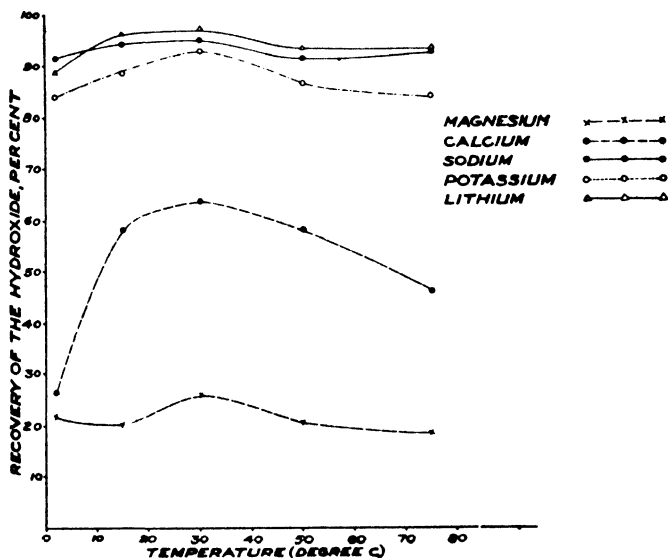



Fig. 50. Effect of Temperature on the Speed of Electrodialysis

Back-Titration Curves of Soils and Humates by Electrodialysis

Electrodialysis offers a neat way of following the titration curves of acidoids backward, as known amounts of bases can be removed in regulated doses and pH value determined at each stage. The back-titration curve of a Ba soil by gradual addition of H_2SO_4 has been described (page 10), and the error introduced by the accumulation of $BaSO_4$ was pointed out. Not only is electrodialysis applicable to all saloids, but the accumulation of any third substance is altogether avoided. The electrodialysis apparatus with the rotating anode used for this study was a slight modification of the one already described. It is shown in Figure 51.

The single-base soils used in this study were prepared from a black cotton soil containing about 5% humus, which was destroyed by alkaline permanganate. As humus was studied separately, this procedure was considered necessary to get a clear idea of the behavior of each. After the destruction of humus the soil was acid-treated and neutralized with different bases. All pH values were

determined with the glass electrode. Na soil was prepared by neutralizing the H soil to different pH values, and back-titration curves were determined in every case. With other bases only the highest pH value was taken. Five grams of each soil were used for electro-

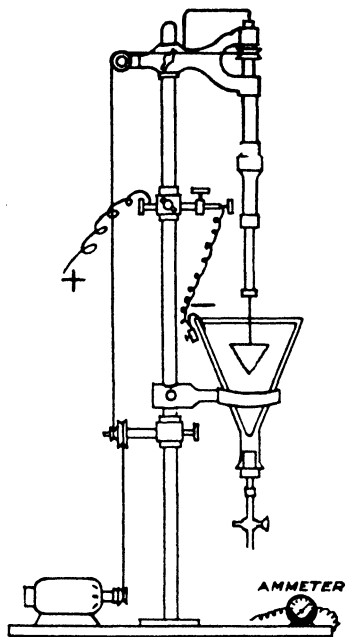



Fig. 51. Apparatus Used for the Electrodialysis of Humates

dialysis. The results are plotted in Figure 52 along with the forward titration curves of the H soil. The remarkable difference in the forward- and back-titration curves at first appeared difficult to explain. It is seen that whatever the initial pH value of the Na soil, it falls rapidly to approximately that of the H soil, even when only 50% of the base has been removed by electrodialysis. Further removal of the base produces but little effect on the pH value. This behavior is shown in a more striking manner where divalent bases are involved, especially with Mg soil, in which the pH drops to the lowest value when only 40% of base is removed by electrodialysis.

Electrodialyzed soil has frequently formed the material of study by various workers when a H soil was required. The ultimate pH value of the reaction of the electrodialyzed soil has also acquired a certain amount of physical significance in soil literature. These results seem to show that unless electrodialysis is carried on for a very long time and proper care is taken to watch the course of the reaction, this method of preparing H soil may easily lead to erroneous conclusions. Dilute acid treatment, on the other hand, is not only quicker but more reliable.

The enormous difference in the forward- and back-titration curves was baffling until the following reasoning was applied: when alkali is shaken with soil, at least 48 hours are required for attainment of equilibrium; therefore, if alkali is removed from the soil, an equally long time must elapse before equilibrium can be established. The soil suspension was therefore shaken for 48 hours, after each incremental removal of alkali, and the pH value determined after shaking. The back-titration curve thus obtained very nearly coincided with the forward curve.

The mechanism of pH changes in the soil due to the addition or removal of alkali may be visualized somewhat as follows: soil aggregates offer a good deal of resistance to their disintegration, and

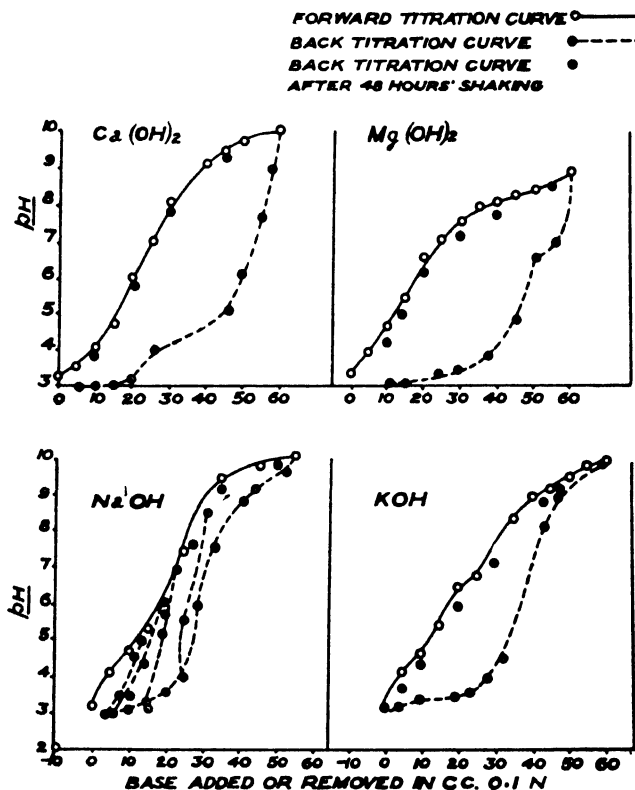



Fig. 52. Forward and Back Titration Curves of Soils

when alkali is added to a soil consisting of such aggregates it attacks the particles nearest it. This results in an unstable state, and particles on the inside of the aggregates slowly take up the alkali to produce a state of equilibrium. The same thing happens when alkali is removed: it comes out mostly from the particles on the outside, which slowly brings the alkali from the inside to equalize the pH value of all the particles. This view, if correct, leads to a very important conclusion, namely, the diffusibility of cations, which

leads to a uniform distribution of the cations throughout the soil mass. It follows also that if this equilibrium is disturbed by the removal of ions from one portion, migration of ions must result. In other words, if plants make use of these bases from the part in immediate contact with the root hairs, more of these bases must travel from other parts to make up the deficiency. Saloids therefore behave like soluble salts in this respect.

Electrodialysis of Humates

Humic acid and humates will be studied in a separate section. The object of including their electrodialysis in this section is to show the similarity in the behavior of soil acidoids and humates.

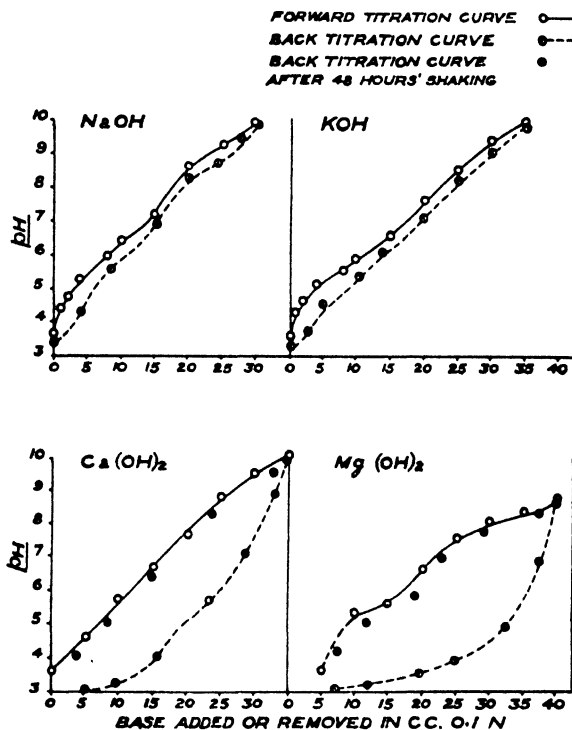



Fig. 53. Forward and Back Titration Curves of Humates

Humates of Na, K, Ca and Mg were prepared by the addition of equivalent amounts of alkalies, followed by shaking for 48 hours. In one set of experiments alkali was removed continuously and the pH value of the residual humate determined. Ca and Mg humates, like the soil suspensions, were also shaken for 48 hours after every removal of alkali. In every case, 0.5 gram of the humate was taken for electrodialysis. The forward- and the back-titration curves are given in Figure 53.

The general similarity between the soil and humus curves is apparent. Likewise, the back-titration curves are identical with the forward curves, provided sufficient time is allowed for the attainment of equilibrium after the removal of any portion of the alkali. It is to be noted that Na and K humates show only a slight shift of the back-titration curves, even without shaking. This is in conformity with the view that humates of alkali metals are soluble in water.

For the electrodialysis of humates of alkali metals, ordinary filter paper is not suitable. Good filter paper impregnated with collodion or parchment paper should be used.

It is convenient at this juncture to point out that some of the alkali, especially the Ca and Mg, displaced by electrodialysis, sticks to the cathode and must be removed by acid treatment every time the alkali is determined. Simple titration of electrodialyzate may lead to very erroneous results. For instance, as little as 10 per cent of the Mg may come down in the electrodialyzate, the rest adhering to the cathode. It is not unlikely that the slower rate of electrodialysis of Ca and Mg may to some extent be due to the fact that some of the hydroxide which remains on the cathode may again react with the acidoid, giving a lower value for these ions.

Reclamation of Alkaline Soils by Electrodialysis

The underlying principle of all the methods of reclaiming alkaline soils is the conversion of the Na soil into a Ca or a H soil; this can be brought about by treatment with a Ca salt or an acid.

The application of electrodialysis for reclaiming alkaline soils is a novel method which holds vast possibilities. Not only are no extraneous chemicals required, but the by-product is sodium hydroxide, which is of economic value. A very important feature of the process is the increased rate of percolation and opening up of the soil. The rate of percolation increases as soon as the electric current is switched on.

Laboratory experiments were first conducted to gain experience. One was in a large Buchner funnel 18 inches in diameter, and the other in a wood box 2 by 3 feet. In the former the usual porcelain sieve of the funnel was replaced by a brass plate which formed the cathode. In the latter five types of cathodes were used:

(a) iron pipe 2 feet long perforated all around;

(b) iron pipe 2 feet long perforated on the upper surface only;

(c) V-shaped wood pipe 2 feet long covered with thin perforated iron sheet;

(d) V-shaped wood pipe covered with perforated brass sheet;

(e) porous tube containing tubular wire gauze as electrode.

Currents ranging from 6 to 14 amperes were passed for varying lengths of time and the experiments were successful on the whole. The most important finding from the laboratory studies was the increased rate of percolation, which continued even after the current was turned off.

Field experiments. A plot of land 15 by 15 feet was trenched all around. The trench was 3.5 feet deep and 1 foot wide. The cathode was an iron tube 6 feet long and 4 inches in diameter with perforations at the top. This was buried in the soil to a depth of three feet by digging a furrow from the center of the plot toward the middle of the trench, with a gentle slope to insure easy flow of water. A ridge about 6 inches high was made around the plot to maintain a certain head of water. The trench was filled with water, and a liberal watering was given at the top to bring about the initial saturation of the soil, after which the water was pumped out of the trench. The anode was a sheet of iron 3 by 6 feet long, laid at the top of the moist soil block just above the cathode. After the initial saturation the plot was watered to a depth of 4 inches. A vessel was placed beneath the protruding end of the cathode in the trench to find the initial rate of percolation, which was practically nil. A current of 22 amperes from a 220-volt main was passed through a suitable resistance. Alkali began to trickle almost immediately and soon formed a thin stream; 2.5 liters were collected in 45 minutes. The strength of the solution was 0.1N. Rains intervened, and the experiment had to be discontinued.

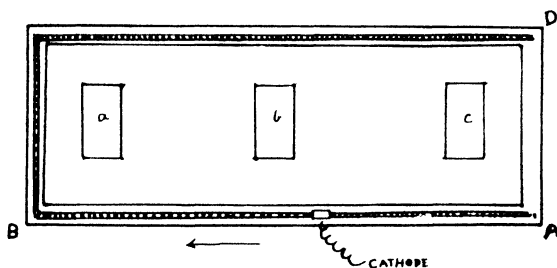



Fig. 54. Electro-Reclamation of Soil - Plan of Field Experiment

One year later, the same electrodes were connected again. During the intervening period the cathode had become choked; therefore, when the current was switched on, the alkali did not come out until after an hour, and even then the rate of percolation was only 300 cc an hour, which fell to 50 cc an hour when the current was turned off. The increase in the rate of percolation was very marked and was tested several times by switching the current on and off. The strength of the alkali coming out was 0.05N against 0.1N obtained in the previous year. The soil, however, had been considerably improved by the first treatment and the rains that followed. To start with, the top 3 inches of soil contained 4.8 m.e. of Na saloid, which fell to 3.5 after 2 hours' treatment and to 2.8 on further treatment for 4 hours. The total current consumed was 5 units.

Next, a field 17 by 50 feet was selected and trenched all around. The anode was a sheet of iron; and the cathode, a twisted wire rope about 1 inch in diameter (a rejected rope of a steam tackle), was laid on the drain on three sides. The plan of the experiment is shown in Figure 54.

A current of 22 amperes with a terminal potential of 153 volts was passed through. When the anode was in position *a*, the total resistance was 7 ohms; at position *b* or *c*, it was 9 ohms. When the area of the anode was increased about 5 times, the resistance fell to 2 ohms. Increasing the area of the cathode did not have very much effect on resistance. A good deal of water was standing in the drain B-C and in two hours the alkalinity of the water rose by 1 m.e. per liter. Because of a slope, there was not much water in the drains A-B and C-D. The alkalinity of a small amount of water collected in a puddle had increased by 6 m.e. per liter as a result of the passing of electric current. The alkalinity of the water around the anode decreased by 1.3 m.e. per liter. During 5 hours of electrodialysis the soil had lost 0.6 m.e. of sodium in the saloid per 100 grams in the top 3 inches.

Before starting these experiments, there were grave misgivings as to the success of the method. It was argued that the soil would act as an infinite conductor, and all the electrical energy would be diffused. Practical trials, however, proved this supposition to be incorrect. The method, it seems, holds promise of practical importance in other directions as well. During the process of electroreclamation, phosphates and nitrates are likely to move to the upper surface, where they will prove useful to plants. This point and the effect on the microbiological population of the soil requires study. The application of $CaSO_4$ together with electric treatment is likely to prove more beneficial than without such treatment. A preliminary experiment in this direction showed a marked decrease in electrical resistance when $CaSO_4$ was applied.

The economics of electro-reclamation have not been studied thoroughly. They depend largely on local conditions, such as the cost of electricity and the value of the land, and must be estimated by individual workers.

A point of considerable interest, both theoretical and practical, arose from these studies, namely, the minimum moisture content of the soil at which electrodialysis can be carried out.

The apparatus shown in Figure 55 proved satisfactory. Cylindrical blocks were prepared by pressing moist soil in a press. These could be held in a clamping device which kept the two sides pressed between the electrodes to insure intimate contact. Two methods of studying the movement of ions seemed possible, namely:

(1) Interposing a wet filter paper pad between the cathode and the soil block. This pad could be separated at the end of the experiment and washed free of the bases removed by electrodialysis.

(2) Pressing a similar block of a H soil against the block under study and joining it to the cathode. The H soil block could then be removed after a definite interval of time and analyzed for cations which had moved into it from the other block. The second method proved more satisfactory and was the one finally adopted.

Single-base soils were prepared from a H soil by neutralization

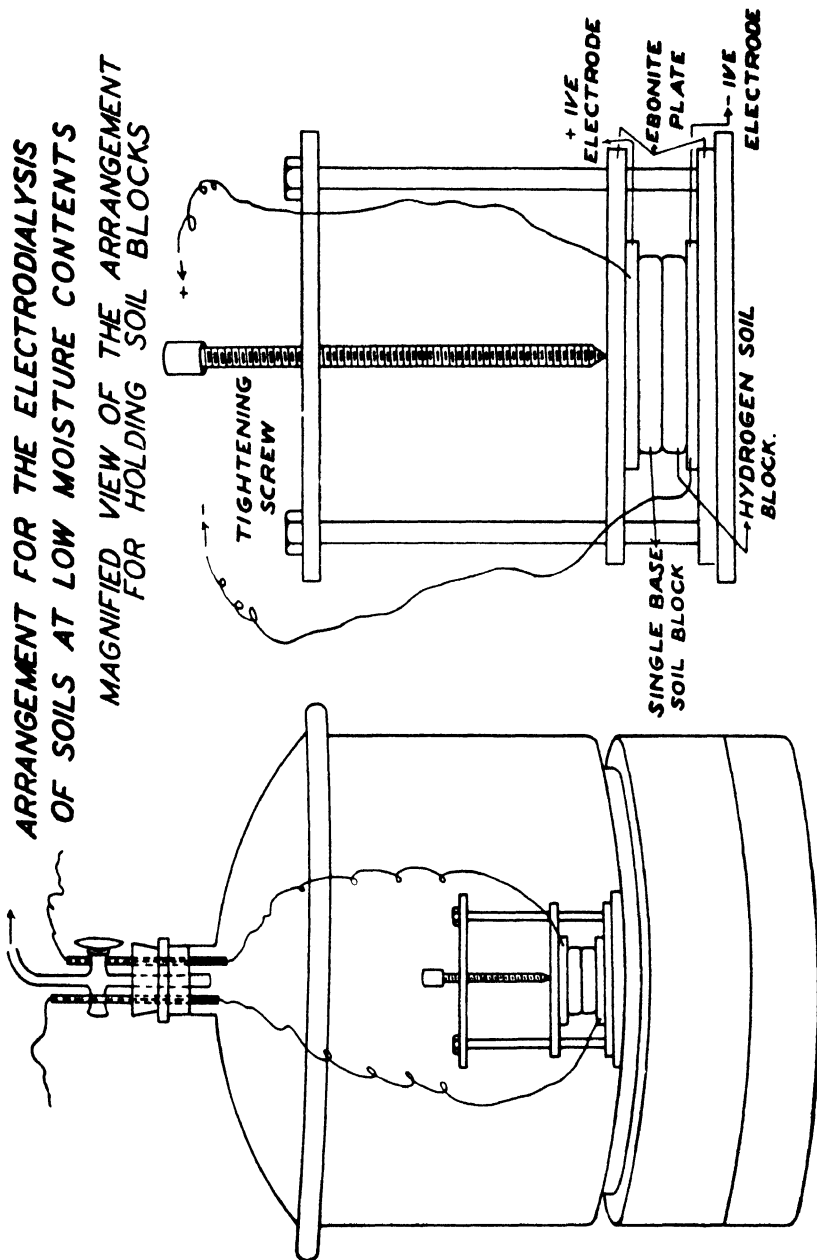



Fig. 55A. Arrangement for Electrodialysis of Soils at Low Moisture Contents
Fig. 55B. Magnified View of Arrangement for Holding Soil Blocks

with appropriate amounts of hydroxides. Ten grams of moist soil were pressed in the mold and kept over sulphuric acid-water mixtures for several days until equilibrium was established. A number of similar sized soil blocks were prepared from 10-gram portions of the H soils and kept in desiccators along with the single-base soil blocks. The electrodialysis was carried out by making the electrode in contact with the H soil block the cathode, and that with the single-base soil block the anode, in vacuum desiccators over sulphuric acid-water mixtures of the same humidity as that with which the blocks had been brought to equilibrium. This was done to insure as far as possible uniform moisture content of the block during the entire electrodialysis. It must be admitted that it would be impossible to maintain a uniform moisture content throughout the experiment because the moisture is continuously moving from the saloid to the acidoid along with the bases. However, by conducting the experiment under vacuum in an atmosphere of definite humidity, it was believed that the bases would be moved toward the H soil by the continuous absorption of moisture by the cylindrical block. In fact, the whole phenomenon could be described as leaching of the bases at low moisture content. The H soil blocks were changed after every 24 hours. The results are given in Table 44.

Table 44. Electrodialysis of Na soil blocks exposed to different humidities

Time of electrodialysis (days)	Current variations (milliamps)	Humidity (%)	Initial moisture content %		Recovery of base (m.e./100 gm. soil)
			H soil	Na soil	
5	60. to 100	10	6.39	4.40	4.70
3	0.4 to 0.5	20	6.78	5.44	5.11
4	0.5 to 1.65	40	9.45	7.60	17.70
4	1.5 to 12.0	50	11.0	8.0	45.92
4	0.6 to 20	60	12.54	9.04	47.89
4	0.5 to 30	70	13.6	14.20	52.84
3	1.8 to 30	80	14.7	15.31	51.07

Sodium soil blocks were used in the first instance. It was found that with 220-volt mains a current of more than 100 microamperes could not be passed when the soil was in equilibrium with 10 per cent relative humidity. The resistance of the soil block decreased considerably when it was brought into equilibrium with 60 per cent humidity, so that a current of 40 milliamperes could be passed. For higher humidities the current was adjusted to about 30 milliamperes by using external resistance. It was noticed, however, that the current passing varied a great deal, and toward the end of the 24 hours it fell to less than one-tenth of the original value. This fall is obviously due to the increased resistance of the soil brought about by the progressive removal of bases.

It is interesting to note that even when the soil is in equilibrium with 10 per cent relative humidity, bases can be removed by elec-

trodialysis. The fact that the rate of removal is extremely slow can be readily understood when we remember that the current passing is only a fraction of a milliampere. In other words, the conclusion is inevitable that the moisture held by the soil at 10 per cent humidity is in no way different from that taken up at higher humidities. This point will be discussed at length in another chapter.

Electrodialysis of Ca and Mg soils was carried out at 50 per cent humidity, in the usual manner. The experiment was repeated with a 1:1 mixture of Na and Ca soil as well as Na and Mg soil. The results are given in Table 45. More Mg and Ca are removed when these

Table 45. Electrodialysis of Na-, Ca, and Mg- soil blocks exposed to 50 per cent relative humidity. (Total period of electrodialysis: 4 days)

Current passed through the blocks (milliamps)	Cation	Base recovered	Base left in soil block	Nature of saloid
0.7 to 12.0	Ca	13.23	33.83	Ca soil block
0.6 to 5.0	Mg	18.65	29.49	Mg soil block
1.5 to 15.0	Ca	12.0	9.8	(Ca + Na) soil block
"	Na	22.8	0.9	"
0.5 to 5.0	Mg	11.26	11.6	(Mg + Na) soil block
"	Na	21.05	2.24	"

elements are alone than when present with Na. The slower rate of electrodialysis of Ca and Mg soils as compared to Na soil has been commented upon in the foregoing. It is remarkable that the behavior of soil in equilibrium with moisture at 50 per cent humidity is similar to that of a suspension as regards electrodialysis. This fact not only emphasizes the continuity of the soil-water system down to extremely low moisture contents, but leads to the important conclusion that the diffusion of bases in natural soils would be possible even when they are in the semi-dry state. It is interesting to note that in the case of Ca-Na and Mg-Na soils, comparatively less Ca is removed in the first 24 hours than subsequently when the major part of the Na has been removed. These results confirm the view that the toxicity of alkaline soils is due largely to the deficiency of Ca brought about by inability of this ion to diffuse out in the presence of Na ions.

A comparison of Tables 44 and 45 will show that comparatively higher currents can be passed through a Na soil block than a Ca or Mg block. The slower rate of electrodialysis of the latter may be partly due to this cause. However, a comparison of results at the same current intensity leaves no doubt that divalent ions have a lower rate of diffusion than monovalent ions. The effect of current intensity on the rate of recovery of Na ions was shown in a striking manner in the case of a Na soil block electrodialyzed at 50 per cent humidity. 1.4 milliequivalents of NaOH were recovered in 24 hours at a current intensity of the order of 60 to 100 microamperes, whereas 5.9 milliequivalents of the base were recovered in the same

time when the current was raised to 1.8 to 2 milliamperes.

From the results given in Table 45 the electrodialysis of Ca and Ca-Na soil blocks does not seem to proceed in a regular manner in some cases, the rate of recovery showing an erratic value. This is due to the extremely slow rate of electrodialysis. Each experiment had to be carried out over a long period during which the current varied greatly and even stopped altogether. No particular point could be gained by a repetition of the experiments under more rigidly controlled conditions, as it would not alter the fundamental conclusions regarding the movement of cations in almost dry soils. For in nature air-dry moisture content would rarely go below that corresponding to a relative humidity of 10 per cent. Even though plants die even at higher moisture contents, the cations continue to move.

CHAPTER XVIII

POLAROGRAPHIC CURRENT-VOLTAGE CURVES AND OXIDATION-REDUCTION POTENTIAL OF SOIL SALOIDS

It is well known that every reduction takes place at a definite voltage which is characteristic of the respective substance, i.e., its reduction potential. If the voltage of the electrolyzing current is lower than the reduction potential, no reduction takes place, and consequently no current passes through the solution. When the requisite potential is reached, the current flowing through the solution is directly proportional to the concentration of the reducible substance. This principle is extensively applied in the polarographic estimation of metals.

The essential parts of the apparatus required for this purpose are a mercury dropping cathode, a 6-volt battery connected to a potentiometer for adjusting a uniformly increasing voltage in the electrolytic circuit, and a microammeter for reading the current flowing in the circuit. The current voltage curve obtained by gradually increasing the voltage and noting the current at every step is characteristic of the nature and concentration of the ions in solution. As in all other respects soil saloids behave like soluble salts, a close analogy between the two sets of polarographic curves would furnish another proof of the similarity of behavior between ions in true solution and those in monomolecular surface solution. Though an automatically operated polarograph is available on the market, a simpler apparatus that can be assembled from parts found in any laboratory is quite satisfactory for the purpose. The apparatus shown in Figure 56 consists of a mercury dropping cathode, a potential divider connected to a 6-volt accumulator, and a microammeter. In the mercury cathode, factors such as the size and velocity of mercury drops, the strength of the solution and the dimensions of the vessel must be kept constant.

A black cotton soil containing 52% of clay was used for these experiments. The current voltage curves for chlorides of Na, K, Li, NH_4, Ca, Ba and Mg were compared with soils neutralized with corresponding bases. The results are plotted in Figures 57 and 58 for Na and Ca only, for the sake of brevity. Curves with other salts and corresponding soil saloids were exactly similar to those shown here, and illustrate in a striking manner the close analogy between saloids and soluble salts.

As H soil is only feebly ionized, very little current passes, even at 4 volts. As it is gradually neutralized, the sharp break at the reduction potential becomes more and more apparent. This observation is in agreement with the general behavior of weak acids, the salts of which are generally much more ionized than the acid itself. The points in the earlier portions of the curves overlap so much that only two lines corresponding to the lowest and the highest concentrations are given, for the sake of clearness. In the first portions of the curves of the chlorides a peculiar kink is noticed which is absent in the curves of the soils. No attempt was made to seek an explanation for this phenomenon, which is not important for the purpose of this study.

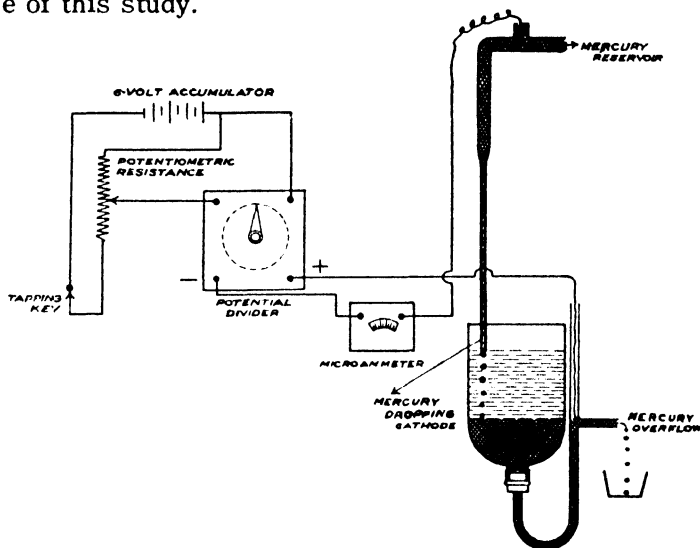



Fig. 56. Diagram of Apparatus for the Polarographic Examination of Soils

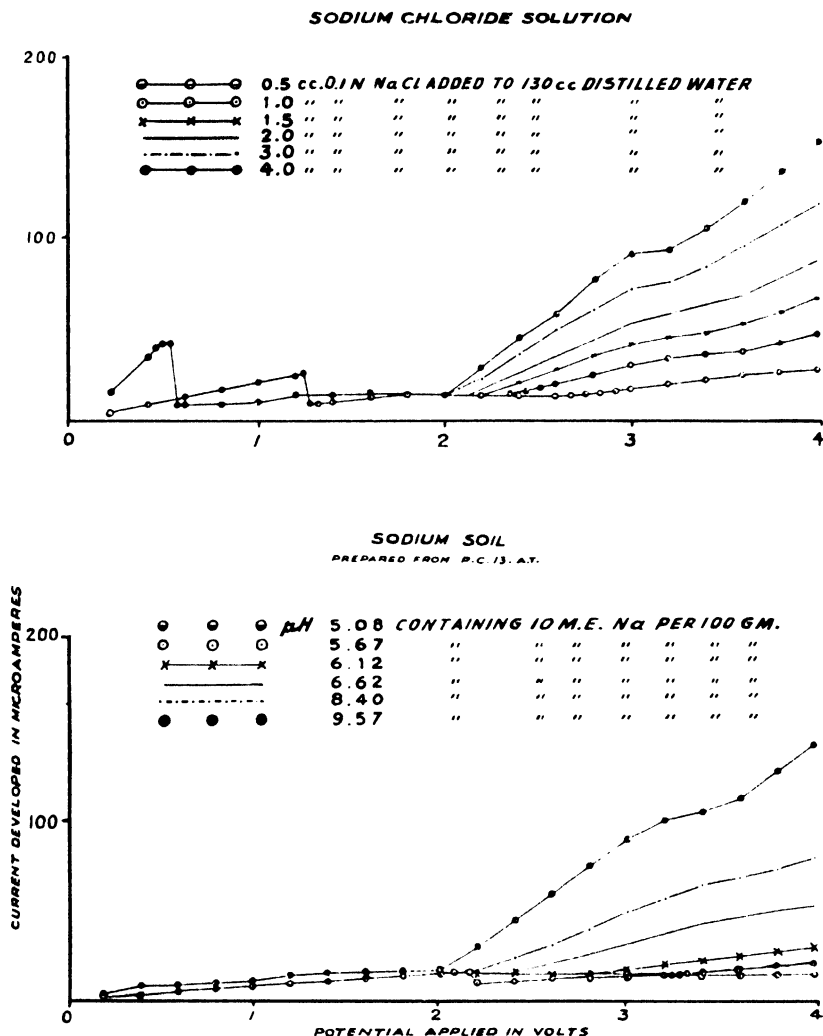
Another interesting point is that soils with monovalent cations are more ionized and consequently give steeper current voltage curves than do soils with divalent cations. This is also in general agreement with the behavior of true salts. The data do not admit quantitative comparison of the degree of ionization of the various cations because, in spite of the precautions taken, fluctuations due to temperature changes and slight alterations in the drop time and in the distance between the electrodes are bound to occur. The experiments leave no doubt, however, as to the fundamental similarity between true salts and soil saloids.

Oxidation-Reduction Potentials in Soils

The fundamental equation involved in oxidation-reduction potentials is:

$$E_h = E_o - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]}$$

E_h is the potential in volts, referred to the normal hydrogen electrode as zero, of the system under consideration; E_o is a constant characteristic of the system and equal to E_h when the ratio $\frac{[Red]}{[Ox]}$ is

Fig. 57. Polarographic Current-Voltage Curves for NaCl Solution and for Na-Soil

unity. [Red] and [Ox] represent the concentrations of reductant and oxidant respectively, and R, T, n and F have their customary significance.

The equation shows E_h to be dependent on the ratio of oxidant to reductant, as well as on temperature and on the particular system under investigation. It is not generally realized that the ratio of

oxidant to reductant is the most important factor in the thermodynamic relation. Wherever a definite potential difference is to be established at the electrode, there must be in the system two species, one of which is the direct or indirect reduction product of the other, and the ratio of their concentrations or activities must

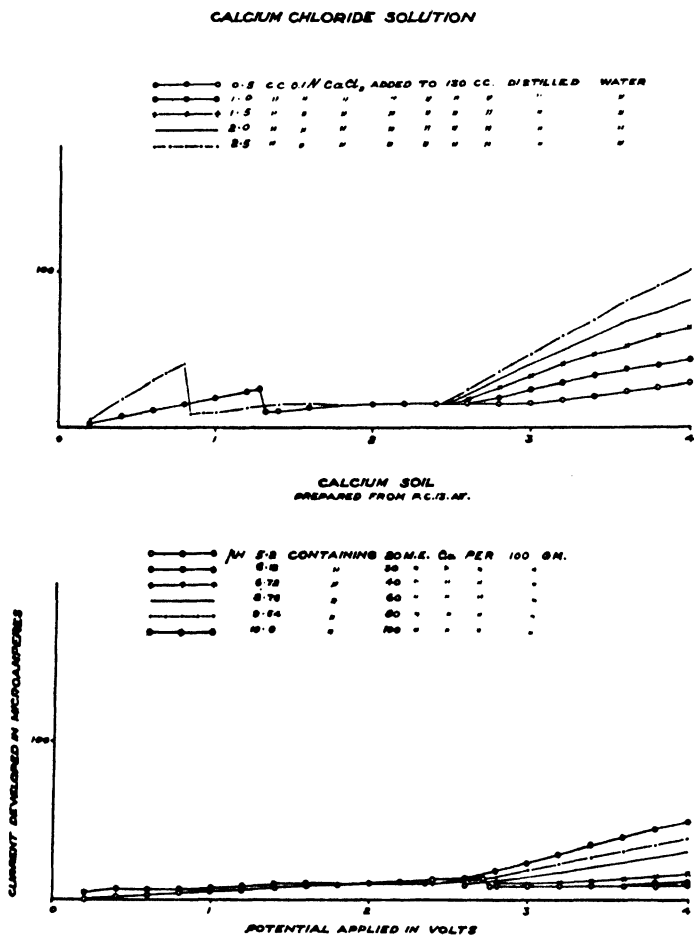



Fig. 58. Polarographic Current-Voltage Curves for $CaCl_2$ Solution and for Ca-Soil

be of finite magnitude. Neglect of this principle is not unusual in soil literature. It must be emphasized that a system that does not reversibly maintain a finite ratio of oxidant and reductant leaves the electrode functioning in a manner that prevents the interpretation of any results obtained. Some potential will always be developed when a clean platinum electrode is dipped into a soil suspension, or in any solution or suspension for that matter; but unless

the thermodynamic equation can be satisfied by the introduction of known components, the results will have no fundamental value and may be meaningless, if not misleading.

The universal presence of iron in all soil systems might reasonably be assumed, and all potentials interpreted in terms of the system $Fe^{+++} + E \rightleftharpoons Fe^{++}$; but we cannot avoid the possibility of the participation of other systems in dealing with a material like soil. The results in this case can be valuable and interpretable only if characteristic data for one particular system can be obtained which preclude interference by another system. The relation between pH and E_h is practically linear for a system in which the ratio $\frac{[Red]}{[Ox]}$ is constant. The relation is complex when both this ratio and pH change simultaneously, and to obtain a complete picture a figure in three dimensions is necessary. Fortunately in soils the only possible system is Fe^{+++}, Fe^{++}, which gives a constant potential for a given ratio, irrespective of the pH value. On the other hand, the range of this system is limited, because at high pH values iron is precipitated. We are therefore confronted with a dilemma in the case of soils.

Table 46. Change in potential in millivolts (slope) for unit change in pH

Soil No.	Slope	Soil No.	Slope	Soil No.	Slope
M Series		P.C. Series		P.C. Series	·
1	59.5	2	68.5	44	57.5
2	58.7	4	37.4	45	68.7
3	66.1	6	69.7	47	27.7
4	44.4	7	56.4	48	39.3
5	43.0	9	54.8	49	46.5
6	63.1	10	48.9	50	67.5
7	56.8	11	41.8	53	65.3
8	51.8	12	68.5	54	56.5
9	67.5	14	51.0	56	31.2
10	60.3	17	55.1	57	61.0
11	53.8	20	53.5	58	35.7
12	46.2	21	47.8	Gelatin	65.6
13	52.2	26	73.1	Humic acid	52.4
14	40.6	27	26.8	Iron silicate	65.0
15	46.0	28	28.8	Aluminum silicate	32.6
16	57.2	29	39.1		
17	63.0	30	65.0		
18	64.5	31	55.4		
19	56.5	33	76.3		
20	56.5	39	64.5		

The thermodynamic relation might be satisfied by the fundamental equation for the system Fe^{+++}, Fe^{++}, but the quantity of iron that can remain in solution above pH 5.0 becomes so small that the system would cease to function as such. In an actual experiment with a black cotton soil shaken with buffer solutions of increasing pH values, the amounts of ferric and ferrous iron brought into solu-

tion at a pH value of 0.65 were 0.1333 and 0.1167, respectively, per 100 grams of soil. These amounts fell to 0.000067 and 0.010 at a pH value of 5.2. As this pH range is almost never found in natural soils, we are forced to the conclusion that this system plays no part in determining the oxidation-reduction potentials in natural soils. However, by eliminating extraneous influences, it might be possible to interpret the oxidation-reduction potentials in soils in terms of some known system.

A number of H soils were shaken with increasing amounts of alkalies and the relation between pH and E_h was determined. This relationship is found to be linear for all soils, irrespective of the nature of the alkali used for titration. Some typical curves showing this relation are given in Fig. 59. The slopes of such straight lines for a number of soils are given in Table 46.

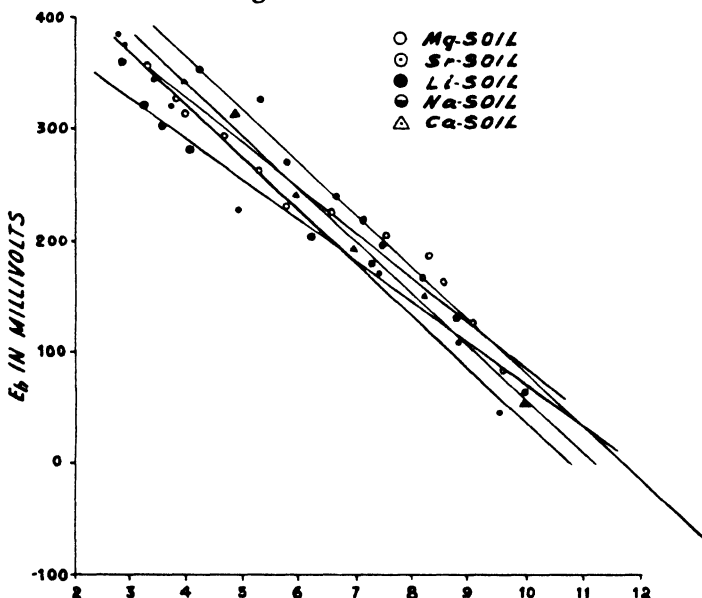



Fig. 59. Relation between pH and E_h of Single-Base Soils

They indicate millivolts of change in potential for every unit change in pH. These values were obtained by the method of least squares, though a less accurate value could be obtained graphically by fitting a straight line to the pH-E_h values. It will be seen that the mean value of slope for all the soils is equal to 53.4 millivolts. In a metallic hydrogen electrode, according to Nernst, the electrode has a tendency to emit hydrogen ions into the solution. On the other hand, the hydrogen ions of the aqueous solution have a tendency to settle on the metallic surface. One or the other tendency prevails, according to the concentration of hydrogen ions in solution. The potential of such a metallic platinum hydrogen electrode shows a change of 58 millivolts for a unit change in the pH value of the solution.

Exactly the same thing happens in a H soil in which the tendency for the hydrogen ions to be liberated and to diffuse into the aqueous solution is even greater. This tendency is gradually diminished as the acidoid is neutralized with a base. Thus the thermodynamic relation is the same and the average value of 53.4 is remarkably close to the theoretical value of 58 millivolts. It is also found that not only is the relation substantially correct for soils, but other substances, like gelatin, humic acid and iron and aluminum silicates, all of which behave as acidoids, give a straight-line relationship between pH and E_h. The slopes of these lines are included in Table 46 and show an average value of 54, which again is very close to theoretical.

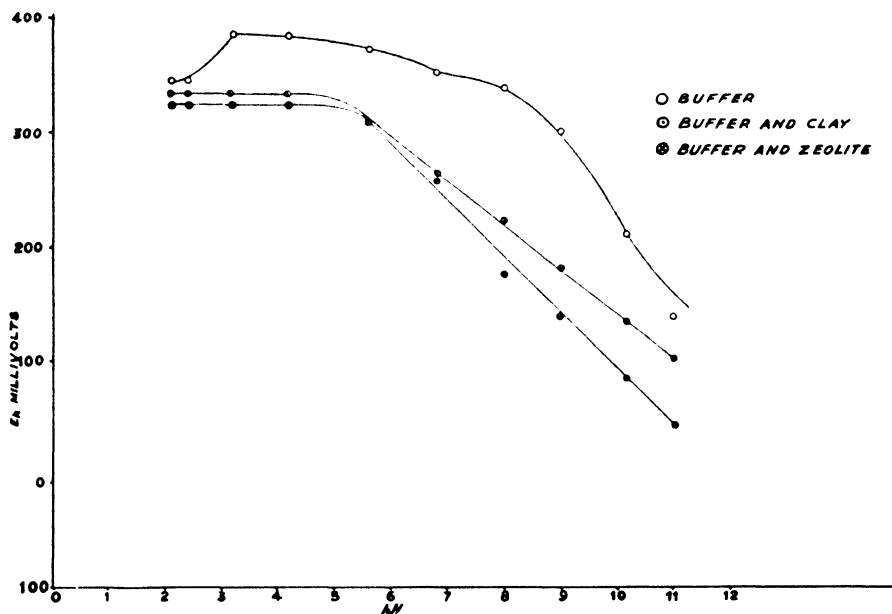



Fig. 60. Stabilization of pH−E_h Relationship by Clay and Artificial Zeolite in Buffer Solution

It will be seen that the thermodynamic relation does not include any factor relating to the quantity of the acidoid, and therefore the pH−E_h relation should be independent of the concentration of the soil suspension. A novel application of this principle is that a small quantity of an acidoid could be used for stabilizing the pH-E_h relation of an ordinary buffer. This will be clear from Figure 60, which gives the pH-E_h relation in a series of buffer solutions before and after the addition of small amounts of clay suspension and finely powdered zeolite (sodium aluminum silicate). The quantities of clay and zeolite added were so small that the pH value of the buffer was not affected, yet the potential was stabilized. It will be recalled that only a small quantity of quinhydrone is required to stabilize the pH-E_h relation in a solution, and this principle forms the basis

of pH determinations by the quinhydrone electrode. Similarly, a small quantity of a colloidal solution that behaves as an acidoid could be used for measuring the pH value of solutions. The possibility of developing such an acidoid electrode for pH measurements should be explored by other investigators. Such an electrode would cover the alkaline range up to pH 10, and would thus be superior to the quinhydrone electrode.

With such perfect relationship between pH and E_h, it is hardly to be expected that the measurement of oxidation-reduction potentials in natural soils could lead to results of any greater value than those that could be obtained by pH measurements.

The fact that there is an appreciable difference of potential between two soils neutralized to a different extent leads to another interesting speculation as to the cause of ionic movements in soils. The mechanism of utilization of saloids by plant roots is still obscure. Two pointers toward a possible explanation may emerge from this study. The pH value of the cell sap in the roots is always kept low by the CO_2 that is produced. This pH value can be stabilized by the colloidal matter acting as acidoid, thus setting up a potential difference on the two sides of the cell wall, driving the cations from the soil saloids into the cell sap.

CHAPTER XIX

ACTION OF CARBON DIOXIDE ON SOILS

Carbon dioxide plays an important role in the economy of nature. Not only is it the means of transporting carbon from one place to another, but by its acidic character, it causes the movement of minerals, the weathering of rocks, and the release of plant nutrients from the soil.

Two things are important in investigating the action of CO_2 on soils: control of the partial pressure of CO_2 and control of the nature and amount of the saloids in the soil. The former is accomplished by the help of gasometers and the latter by simply neutralizing a H soil with different bases up to various pH values. The air containing CO_2 is forced through the soil suspension held in a funnel with a sintered glass disc. Two standards were adopted: namely, 1 per cent CO_2 and 100 per cent CO_2.

The main effect of CO_2 on soils, and the one that is of greatest interest from the practical point of view, is associated with alterations in the soluble salts and in the pH values. Twenty-five soils were used for this study. Only CO_2 was passed through the suspension, which had a soil-water ratio of 1:10. The pH values were determined with the glass electrode. The results, given in Table 47, show that the soluble salts increased and the pH value decreased, the extent of the change being different for different soils. The ratio of the pH values before and after the passage of CO_2 is, however, fairly constant (approximately 0.7) but is slightly higher for soils containing no $CaCO_3$ than for calcareous soils. The ratio of soluble salts before and after treatment is not constant. There is some indication, however, that this ratio is higher for carbonate-free soils than for those containing $CaCO_3$. The effect of CO_2 on soluble salts is similar to that of soils. Results with a few salts are included in Table 47 and the ratio pH_2/pH is of the same order as in the case of soils. Action of CO_2 on acidoid progressively neutralized with different bases was studied by passing CO_2 through suspensions. The results are given in Table 48.

It is seen that Na soil is not flocculated by CO_2. At lower pH values the flocculation is only partial. The ratio of pH_2/pH decreases as the original pH increases, irrespective of the nature of the base in the soil.

Table 47. Effect of CO_2 on pH and on soluble salts of soils

SOIL P.C.	CLAY 0.002 MM.	CARBONATE	INITIAL pH (pH_1)	pH AFTER PASSAGE OF CO_2 (pH_2)	$\frac{pH_2}{pH_1}$	SALTS BEFORE PASSAGE OF CO_2 (S_1)	SALTS AFTER PASSAGE OF CO_2 (S_2)	$\frac{S_2}{S_1}$
	per cent	*per cent*						
1	11.30	34.25	8.08	5.70	0.70	0.26	0.75	2.88
2	59.35	5.0	7.90	5.64	0.71	0.42	0.66	1.57
3	62.2	0.5	7.37	5.22	0.70	0.078	0.40	5.12
4	15.2	1.0	8.48	5.6	0.66	0.11	0.5	4.54
5	12.3	1.87	8.8	5.9	0.67	0.078	0.66	8.46
6	28.4	0.0	5.42	4.25	0.78	0.26	0.70	2.69
7	21.8	6.5	9.46	5.8	0.61	0.93	1.8	1.93
8	25.2	0.75	7.7	4.7	0.61	0.13	0.44	3.38
9	21.6	0.0	5.6	4.4	0.78	0.084	0.15	1.78
10	35.6	1.12	7.9	5.2	0.65	0.198	0.73	3.68
11	32.8	2.5	7.5	5.2	0.69	0.18	0.93	5.16
12	7.2	0.0	5.9	4.1	0.69	0.27	0.36	1.33
13	58.9	1.5	7.5	5.0	0.66	0.16	0.54	3.37
14	21.5	0.0	5.57	4.8	0.86	0.05	0.18	3.60
15	22.4	0.25	7.14	5.1	0.71	0.28	0.45	1.60
16	8.7	1.87	7.6	5.35	0.70	0.20	0.66	3.30
17	14.1	0.5	7.3	4.8	0.65	0.30	0.49	1.63
18	22.6	0.12	5.62	4.48	0.79	0.09	0.15	1.66
19	42.6	1.0	7.27	5.22	0.71	0.22	0.44	2.00
20	8.1	0.12	5.74	4.32	0.75	0.07	0.14	2.00
21	13.5	2.87	7.2	5.4	0.75	0.22	0.68	3.09
22	15.1	0.12	5.9	4.74	0.80	0.11	0.23	2.09
24	9.7	1.75	7.32	5.42	0.74	0.13	0.82	6.30
25	4.0	0.0	5.8	5.8	1.0	0.05	0.29	5.80
26	22.5	0.0	6.4	5.8	0.79	0.16	0.29	1.81
Sodium acetate			7.6	5.77	0.75	....	....	....
Sodium biborate			8.86	6.66	0.75	....	....	....
Sodium urate			8.92	6.64	0.74	....	....	....
Sodium carbonate			10.7	6.92	0.65	....	....	....

Carbon Dioxide in Soil Reclamation

The action of CO_2 on soils at once raises the question of the role of CO_2 in the reclamation of alkaline soils. Alkaline soils have the following characteristics:

(a) high content of sodium saloid;

(b) high pH value;

(c) a state of deflocculation or dispersion.

Reclamation of such soils naturally brings about a change in the reverse direction. We shall therefore see to what extent these changes can be brought about by CO_2 in soils of varying degrees of alkalinity. Calcium carbonate is an important constituent of the majority of alkaline soils; the action of CO_2 therefore was studied with and without $CaCO_3$.

Soils of varying degrees of alkalinity at different pH levels were prepared by neutralizing the H soil with varying quantities of $Ca(OH)_2$ – NaOH mixtures of appropriate strength. The results as

Table 48. Action of CO_2 on single-base soils at various pH levels

SOIL	INITIAL pH (pH_1)	pH AFTER PASSAGE OF 1 PER CENT CO_2	pH AFTER PASSAGE 100 PER CENT CO_2 (pH_2)	FLOCCULATION*	pH AFTER ADDITION OF $CaCO_3$	pH AFTER PASSAGE OF CO_2	$\frac{pH_2}{pH_1}$
m.e./100 gm.							
K-Soil:							
39	5.75	5.55	5.18	F	6.45	5.83	0.90
51	7.2	5.8	5.6	F	6.6	6.27	0.77
77	9.83	6.8	6.06	F	7.55	6.53	0.61
Na-Soil:							
20	4.32	4.32	4.24	X	7.08	6.26	0.98
48	6.7	7.1	5.5	X	7.82	6.2	0.82
72	9.25	6.27	6.03	X	6.95	6.28	0.65
Ca-Soil:							
34	3.94	3.83	3.82	PF	No $CaCO_3$ added to		0.96
56	5.97	5.8	5.8	F	calcium soil		0.97
96	9.6	6.8	6.1	F			0.63
Mg-Soil:							
34	5.5	4.5	4.6	PF	5.02	4.78	0.83
56	7.06	6.35	5.47	F	7.15	5.7	0.77
100	8.2	6.6	5.9	F	7.8	6.4	0.71

* F = flocculated; PF = partly flocculated; X = no flocculation.

expressed in terms of the percentage of sodium in the total bases (Ca and Na) present in the soil are given in Table 49.

Table 49. Effect of CO_2 on soils of different degrees of alkalinity

NaOH	$Ca(OH)_2$	DEGREE OF ALKALINITY	INITIAL pH (pH_1)	pH AFTER PASSAGE OF 1 PER CENT CO_2	pH AFTER PASSAGE OF 100 PER CENT CO_2 (pH_2)	FLOCCULATION*	pH AFTER ADDITION OF $CaCO_3$	pH AFTER PASSAGE OF CO_2	$\frac{pH_2}{pH_1}$
m.e./100 gm.	*m.e./100 gm.*	*per cent*							
0	12	0	5.80	6.02	5.2	F	....	....	0.89
1.6	6.4	20	5.86	5.67	5.26	F	6.58	5.77	0.89
3.2	4.8	40	5.86	5.86	5.4	F	6.47	5.86	0.92
4.8	3.2	60	5.95	5.8	5.4	F	6.4	5.85	0.90
6.4	1.6	80	6.0	5.86	5.25	F	7.0	6.0	0.87
8	0	100	6.5	5.5	5.25	F	6.9	5.9	0.80
0	18	0	6.0	6.38	5.02	...	....	....	0.83
3.2	12.8	20	6.2	5.55	5.4	F	6.32	5.85	0.87
6.4	9.6	40	6.4	6.2	5.4	PF	6.38	6.0	0.84
9.6	6.4	60	6.4	5.7	5.5	PF	6.43	5.87	0.85
12.8	3.2	80	6.6	5.36	4.58	PF	6.28	5.8	0.69
16	0	100	7.33	5.06	4.62	PF	6.38	5.9	0.63
0	50	0	8.3	7.55	5.8	F	....	....	0.69
8	32	20	8.6	7.5	5.6	F	6.9	5.8	0.65
16	24	40	8.8	6.17	5.6	F	6.6	5.8	0.63
24	16	60	9.1	7.35	5.78	PF	6.8	6.1	0.63
32	8	80	9.35	6.75	6.1	PF	7.54	5.9	0.65
40	0	100	9.5	6.5	6.0	X	7.2	6.18	0.64

* F = flocculated; PF = partly flocculated; X = no flocculation.

The following conclusions regarding the action of CO_2 on alkali soils are drawn as a result of this study. (a) There is a substantial decrease in the pH value at all degrees of alkalinity, as indicated by the percentage of NaOH in the mixtures of hydroxides. (b) At low pH values flocculation occurs at all degrees of alkalization. When the pH value is high, flocculation fails to take place at degrees of alkalinity higher than 60 to 80 per cent. (c) In the presence of $CaCO_3$, a large amount of Na saloid is converted into Ca saloid with the production of sodium bicarbonate, which can be leached out, resulting in a substantial reduction in the degree of alkalization.

The laboratory results are substantiated by a number of field observations on alkaline soils. It was found that in a rice field the

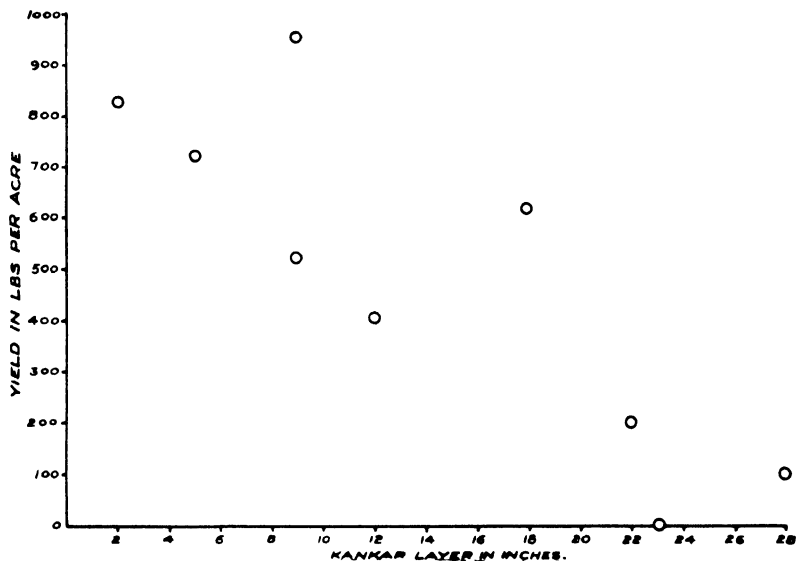



Fig. 61. Relation between Yield of Rice and Depth of Kankar Layer

pH values of soil samples taken from near the roots were lower by more than 1 pH unit than those of the soil taken from some distance away. Similar results were obtained in a field under grass.

The morphological characteristics of alkaline soils in the tropics are not sufficiently defined to serve as a basis of soil classification; for this purpose physicochemical measurements are more suitable. A typical profile consists of three well marked layers: (1) an upper highly alkaline layer, compact and impervious; (2) a layer of medium alkalinity containing $CaCO_3$ nodules (calcareous layer); (3) a layer with a lower alkalinity and higher permeability than (1) and (2). Below the third layer sand usually occurs; from an examination of several profiles it was concluded that alkalinity decreases from the surface downward, and there is generally a sharp break in the calcareous layer. The soil underneath the calcareous layer has a lower alkalinity and clay content than the layers above. Calcium

saloids vary in the opposite direction; they are generally low in the surface layer and increase with depth.

A close examination of these profiles throws considerable light on the mechanism of $CaCO_3$ formation in alkaline soils. The observed facts can be most satisfactorily interpreted by the hypothesis that the underground water containing calcium bicarbonate in solution deposits $CaCO_3$ on coming into contact with alkaline Na clay. At the same time Na clay is converted into Ca clay and the sodium carbonate thus formed travels upward, increasing the alkalinity of the upper soil layer. In extreme cases this may reach the surface. The replacement of Na by Ca in the clay, which accompanies the calcareous layer formation, is a process that may be regarded as the natural regeneration of alkaline soils.

It follows from the above that the nearer the calcareous layer is to the surface, the farther this regeneration has been carried upward. In other words, the nearer the regenerated soil is to the surface, the more readily it would respond to artificial methods of reclamation. A confirmation of this view was obtained from a study of soil profiles from a Reclamation Farm in the second year from the commencement of reclamation work. The yield of rice from the various sub-plots shows a good correlation with the depth of the calcareous layer from the surface. This will be seen from Figure 61.

CHAPTER XX

MEASUREMENT OF pH VALUES OF SOILS

One of the most important measurements in soil chemistry is the determination of the pH values. As has been pointed out before, the pH values of natural soils represent single points on their titration curves and thus fix the saloid-acidoid ratio, which defines completely the behavior of the mixture as a weak electrolyte. Although all students of modern physical chemistry are familiar with methods of measuring the pH values of solutions, a brief description of the various methods may be useful. The methods may be considered under two main heads – electrometric and colorimetric.

Electrometric Methods

All electrometric methods depend on the potentiometric measurements of the E.M.F. developed when the various electrodes are dipped in the solution under examination. This E.M.F. results from the difference of electrical potential between the electrode and the solution, the magnitude of which depends on the concentration or activity of the H ions in solution, and the electrolytic solution pressure of the electrode. The quantitative relation between these two factors and the potential of the electrode has been worked out by Nernst.

Hydrogen Electrode. A noble metal coated with platinum black which will hold large quantities of hydrogen behaves like a hydrogen (H) electrode. In other words if we have two H electrodes in two solutions differing in pH value by one unit, the difference in potential between the two will be 59 millivolts. We can, therefore, have a simple arrangement by which a solution of known pH value is used against an unknown. The E.M.F. of this will enable us to calculate the pH value of the unknown. Instead of setting up two H electrodes, one of which is a known standard, it is generally more convenient to replace the standard H electrode by a more permanent "half cell", such as the calomel electrode. This is an electrode of mercury covered with calomel in the presence of KCl solution, which may be N/10,N, or saturated, the last-named strength being most widely used. If this saturated calomel electrode is used, a tube containing saturated KCl is led directly to the solution in the H electrode vessel. The mercury of the calomel electrode is 0.246 volt more positive than the platinum of the normal H elec-

trode; therefore the pH value of a solution using the calomel electrode is given by

$$pH = \frac{\text{Observed E.M.F.} - 0.246}{0.0591}$$

The actual measurement is carried out by means of a potentiometer and a sensitive galvanometer. For very accurate work a lamp-scale galvanometer is used; for most purposes a unipivot galvanometer is quite suitable. Hydrogen is constantly bubbled through the solution and over the electrode during measurement. The electrodes should not be left in the circuit for more than an instant and for this purpose a tapping key is used. For less accurate work, especially for electrometric titrations, the potentiometer-voltmeter method is used, with a suitable rheostat instead of a potentiometer. An accumulator sends a current across the rheostat, in parallel with which is a sensitive voltmeter. When the sliding contact has been moved to the position which indicates that no current is passing through the galvanometer, the potential difference corresponding to that of the test cell is read off from the voltmeter.

The hydrogen electrode is the ultimate standard of all measurements of H ion concentration, whatever method may be employed in practice. All other electrodes must be checked and calibrated with the help of the H electrode. For practical purposes, however, its use is very inconvenient. Not only is the electrode likely to behave erratically or go out of action without any apparent cause, but the constant stream of hydrogen is difficult to maintain for routine work. Search for a more convenient method resulted in the other well known electrodes.

Quinhydrone Electrode. The oxidation-reduction reaction which takes place between hydroquinone and quinone could be used to measure pH value by dissolving some quinhydrone in the solution under examination and measuring the potential established between the solution and some unattackable metal, such as gold or platinum, by connecting the solution to some standard electrode through a saturated KCl bridge. Instead of using a standard calomel electrode, it is often more convenient to use another quinhydrone electrode in a buffer solution of known pH. In this case

$$pH = K + \frac{E \text{ observed}}{0.0577} \text{ at } 18^{0}C$$

The value of K depends on the pH of the buffer solution used as the standard quinhydrone electrode.

Glass Electrode. If we regard soft soda glass as a solid solution of silica in glass, it can behave like a H electrode because the H ion concentration of the glass phase is held relatively constant by the buffer action of the glass. If two solutions having different concentrations of H ions are separated by a thin glass wall, there

exists a difference in potential between them urging the movement of H ions through the glass in one particular direction, and

$$E.M.F. = 0.058\ (pH_2 - pH_1)$$

where pH_1 and pH_2 are the pH values of the solutions on the two sides of the glass septum. In practice a thin bulb of special soda glass is filled with a solution of known pH value, into which is dipped a special calomel electrode with a minute hole for electrical connection. This glass bulb is dipped in the solution under examination and connected with a calomel electrode through a KCl bridge as usual. On account of the extremely low conductivity of glass, special potentiometers with valve amplifiers are used to amplify the current.

Metal Oxide Electrodes. A metal electrode dipping into a solution in which some of its oxide is placed so as to saturate the solution with the hydroxide sets up potentials depending upon the pH value of the solution. Its potential alters by 58 millivolts for a change of one pH unit. Some metals are so readily oxidizable that they become covered with an oxide film as soon as they are dipped in a solution, and thus behave as hydrogen electrodes, e.g., Al, Zn, Cd and Sb. Of these only the last has found extensive practical application. A clean, polished antimony rod is dipped in the solution under examination and connected to a calomel electrode with a KCl bridge as usual. The antimony electrode is first calibrated against some standard electrode. Instead of a calomel electrode another antimony electrode in a buffer solution of known pH value can be used for measurement.

Colorimetric Methods

The colorimetric determination of pH value is based on the principle that if an indicator added to different solutions assumes the same transition shade the solutions are supposed to have the same pH value. To the solution the pH of which has to be determined, a measured volume of a suitable indicator is added and the color compared with that of the same indicator in solutions of known pH. The method, therefore, depends upon the correctness of the standard reference solution and the choice of the indicator. Standard buffer solutions for colorimetric work generally consist of mixtures of some acids and their alkali salts. The best known are those designed by Clark and Lubs, and are composed of phthalates, phosphates and boric acid. Reference may be made to the universal buffer mixtures, the best known of which is that by Prideaux and Ward. It gives a pH range from 2 to 11.8 and consists of a mixture of phosphoric acid, phenyl acetic acid and boric acid. A selected set of indicators, mostly derivatives of sulphonphthaleins covering the entire pH range, is used. Usually 2.4% stock solutions of the dye are kept and these are diluted when required. The diluted solu-

tion is used for testing, for which purpose 5 drops of the indicator added to 10 cc of the solution are sufficient, and this ratio is kept constant.

The first step toward finding the pH value of an unknown solution is to determine its approximate pH in order to ascertain within which range it lies and which indicator should be used. This can be done by the use of what is known as universal indicators. Having ascertained the approximate pH of the solution, we proceed to its exact estimation. For this purpose one of two procedures may be adopted: namely, (a) with buffer solutions and (b) without buffer solutions.

(a) For this purpose resistant glass test tubes of convenient size are used; these can be held in a comparator for color matching. The test tube containing the unknown solution with 5 drops of the approximate indicator is compared with a series of buffer solutions covering the approximate range of the unknown and treated in exactly the same manner. Sometimes sealed test tubes colored with the indicators are used for matching.

(b) This method is based on the principle that within the pH range of any indicator its color depends on the proportion of the acid and alkaline shade of color. Thus the color of the unknown solution with an indicator is compared with the increasing proportions of the acid and alkaline colors of the same indicator. This can be done by filling the two forms of the indicator in two glass wedges of equal size placed in such a position that they can be moved up and down; thus the various ratios of the acid and alkaline forms can be viewed in small segments and matched with the unknown solution. Reference may be made to other methods useful for approximate work, where the transition colors of various indicators are imitated by suitable mixtures of stable colored salt solutions or colored glass discs.

All these methods have been applied in the case of soils and have been found satisfactory in varying degrees. A careful examination of the literature would indicate that the fault does not lie in the methods but in the fact that soil acidoids and saloids, though behaving in every way like soluble acids and salts, have certain peculiarities, which must be taken into account when recommending a particular method.

We must not forget that soil acidoids and saloids are weak electrolytes, and as such must be sensitive to slight variations in experimental technique, such as soil-water ratio; the nature and amount of salts; the presence of CO_2 in the water; the time of shaking with water, etc. The effect of CO_2 we have already discussed; the time of shaking has been shown to be 48 hours for all studies of pH measurement in connection with titration curves. A slow progressive change may still be going on after even 48 hours' shaking.

The influence of salts and soil-water ratio on soil reactions has been studied by several workers. Most of this work relates to natural soils, in which the nature of the saloids and the soluble

salts present were unknown entities. The results, therefore, were bound to be erratic.

Since the pH value of a soil is due to the surface ionization of the acidoid and the hydrolysis of the saloids, it is reasonable to suppose that the presence of a salt (common ion) would reduce hydrolysis and result in lowering the pH value. On the other hand, since the ionization is confined to the surface, mere dilution in the absence of salts may have no marked effect on the pH value of the suspension as a whole. The experimental evidence in support of this contention was derived from experiments with H soils neutralized to different pH values with various hydroxides. The pH values were determined by the glass electrode.

Effect of Soil-Water Ratio

The results of the study of the effect of soil-water ratio, given in Table 50, show that the same pH is obtained for a given soil even

Table 50. Effect of soil-water ratio on pH of single-base soils

SOIL-WATER RATIO	1	2	3	4	5	6
			pH values of Na-soil			
1:5	5.70	8.44	9.18	9.94	10.36	....
1:6	5.64	8.42	9.16	9.83	10.38	....
1:7	5.63	8.43	9.14	9.75	10.34	....
1:8	5.63	8.42	9.16	9.76	10.38	....
1:10	5.63	8.43	9.22	9.79	10.38	....
1:12	5.63	8.40	9.16	9.82	10.38	....
1:14	5.63	8.71	9.11	9.80	10.40	....
1:19	5.66	8.48	9.19	9.85	10.39	....
1:25	5.81	8.48	9.18	9.87	10.38	....
			pH values of K-soil			
1:5	4.80	6.06	7.40	8.81	9.29	9.86
1:6	4.50	5.68	7.28	8.70	9.44	9.88
1:7	4.50	5.69	7.08	8.72	9.44	9.86
1:8	4.50	5.66	7.10	8.67	9.48	9.87
1:10	4.50	5.69	7.13	....	9.41	9.90
1:12	4.50	5.71	7.28	....	9.48	9.90
1:14	4.58	5.69	7.15	....	9.50	9.94
1:19	4.58	5.71	7.37	8.56	9.50	10.00
1:25	4.80	5.70	7.68	8.86	9.56	9.98
			pH values of Ca-soil			
1:5	4.62	5.26	5.64	6.25	7.10	8.75
1:6	4.59	5.22	5.60	6.24	7.14	8.73
1:7	4.53	5.23	5.62	6.26	7.13	8.62
1:8	4.53	5.20	5.60	6.26	7.11	8.62
1:10	4.64	5.27	5.62	6.28	7.12	8.59
1:12	4.70	5.23	5.61	6.29	7.14	8.69
1:14	4.85	5.24	5.64	6.26	7.18	8.60
1:19	4.82	5.21	5.64	6.34	7.11	8.56
1:25	4.86	5.30	5.62	6.33	7.16	8.58

when the soil-water ratio is varied from 1:5 to 1:25. Erratic values occur here and there, but they do not in any way affect the general conclusion: that even a five-fold dilution has virtually no effect on soil reaction. It is noteworthy that other workers have found that the effect of soil-water ratio is greatly reduced in magnitude when the soil is leached with water and redispersed after most of the soluble salts have been removed. The results with soils neutralized to higher pH values are of interest, because in these soils a certain amount of hydrolysis might be expected as a result of dilution; but even in them the effect of dilution is not noticeable.

Effect of Salts

The effect of salts was studied by using chlorides of various ions, the corresponding metallic chloride being used for every cation in

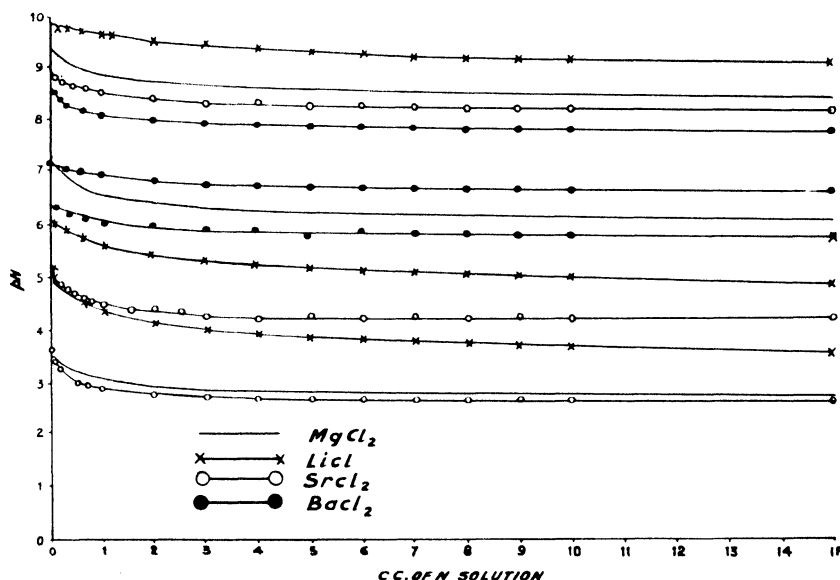



Fig. 62. Effect of Magnesium, Lithium, Strontium, and Barium Chlorides on the pH Values of their Corresponding Soils

the soil. Ten-gram portions of soils at different pH values were suspended in 50 cc of water and normal solutions of the corresponding chlorides were added in 1-cc lots up to 50 cc. The addition of these solutions undoubtedly caused some dilution of the suspension, but as we have seen that dilution alone has no effect on pH, this was ignored. It was also ascertained by direct experiment that results are substantially the same when increasing quantities of salts in the solid state are added. Results for Mg, Ba, Sr and Li are plotted in Figure 62; those for Na, K and Ca are similar.

All the curves obtained being similar, only a few are given by way of illustration. An initial rapid fall is followed by a more gradual one. The initial fall is greater in the acid range and becomes less when the pH is high. When the curves are plotted on a

semilogarithmic scale, a series of parallel straight lines results, the slope of which is characteristic of the basic radical. The following relations are found to hold for various soils:

$$pH - pH_0 = K \log C$$

where pH_0 is the initial pH without any salt; C is the concentration of the salt in milliequivalents per 100 grams of soil, and K is a constant characteristic of the cation. The values of K for the various ions are as follows: Li = 0.30, Na = 0.79, K = 0.55, Ca = 0.48, Mg = 0.48, Ba = 0.26, Sr = 0.28.

It is to be remembered that the effect of salts in lowering the pH values of soils is analogous to a similar effect in ordinary buffer solutions. For instance, the pH value of sodium carbonate-bicarbonate mixture is less in the presence of KCl than in its absence.

A closer study of these results presents some interesting aspects which would offer a rational explanation of the discrepancies observed by previous workers in the effect of soil-water ratio on pH values. It is clear that in the steeper portion of the curve a very low concentration of salts, as would be ordinarily found in most normal soils, would materially alter the pH value. Since this effect does not depend on the absolute quantity of the salt, but rather on its concentration in a suspension, dilution will have the effect of raising the pH value, and the magnitude of this change will be governed entirely by the nature and quantity of the salt present in the soil. These results also lead to the conclusion that measurements of the pH values of soils in N KCl solution would give more reproducible results in the hands of different workers, for not only would the effect of soil-water ratio be negligible, but day-by-day variations in natural soils which are obviously due to changes in salt content would disappear, and the pH value of a soil would assume the importance of a fundamental constant. Alternately, pH value should be determined after leaching the soil free of salts, and is reported as such. This leaching may be done with alcohol to prevent hydrolysis of the saloids. The effect of leaching was studied on twenty soils, from which the following conclusions can be drawn:

(1) The pH value of the leached soil is always higher than that of the unleached soil.

(2) This difference becomes inappreciable when pH is determined in N KCl.

(3) The effect of KCl in lowering the pH value is greater in the leached than in the original soil.

(4) The difference between the change in pH value due to KCl in the leached and in the unleached soil is of the same order as the rise in the pH value of the original soil due to leaching.

The effect of a slightly soluble substance like $CaCO_3$ on soil reaction needs special attention. It is conceivable that even in the absence of other salts, $CaCO_3$ would modify the reaction, even in the presence of N KCl. This was actually observed both in natural

Ca soils, and in soils to which $CaCO_3$ was added and which without it had shown no effect of soil-water ratio in N KCl. The effect of soil-water ratio persists even in N KCl in soils containing $CaCO_3$. For such soils, therefore, the soil-water ratio will still have to be defined even when pH values are determined in N KCl.

The effect of $CaCO_3$ in modifying the pH value of the Ca saloid was already commented upon when dealing with the interaction between $CaCO_3$ and soil acidoid. Or perhaps it would be more appropriate to say that the effect is mutual, so that the pH value of the mixture is lower than that of each individually. As a general rule, the pH value of a Ca saloid in the presence of excess $CaCO_3$ is of the order of 7. If it is higher, the presence of Na saloid must be suspected.

It would be clear from the foregoing that there is nothing fundamentally wrong with the methods of determining pH value, but the latter is so susceptible to environmental changes that fluctuations are to be considered normal. It is true, perhaps, that these fluctuations may be above or below a mean value which may be nearer the one given by the leached soil. Here again we are not absolutely on safe ground, as we are not justified in assuming that we have not altered the acidoid-saloid ratio by leaching. On theoretical grounds, every soil should have a fixed pH value determined entirely by the saloid-acidoid ratio, depending of course on the nature of the cations. Actually our methods of measurement give a value which fluctuates with alterations in the experimental conditions. The need for an absolute method of pH measurement was felt, and the search for it led to a simple solution pointed out by the following assumptions, the truth of which has already been supported by a mass of experimental evidence brought forth in the foregoing.

(a) The pH value of every soil in nature represents a single point on its titration curve, governed by the state of its neutralization with bases. It is, therefore, a buffer mixture of a definite proportion of acidoid-saloid which determines its pH value.

(b) Soil, if shaken with a buffer solution, will have its acidoid-saloid equilibrium point shifted toward that of the buffer solution. In other words, it will take the basic portion from a buffer solution of higher pH value and give its basic portion to one with a pH value lower than its own. Consequently, when no change in reaction occurs, the soil and the buffer are isohydric, i.e., the pH value of the soil is equal to that of the buffer solution.

It is to be remembered that when a soil is shaken with water, it hydrolyzes and some of the cations go into solution as hydroxide. Since the amount of the hydroxide going into solution depends on the state of neutralization, or pH value, of the soil, and since the actual amount of the base removed from the soil and going into solution is very small, the pH value of the water approximates that of the soil. In natural soils, however, this ideal condition is seldom attained, as there is always some salt present, which can suppress

this hydrolysis, thus lowering the pH value. The ideal method, therefore, would be one in which no hydrolysis is allowed to take place. In the isohydric method, this state of affairs is realized by interpolation, for, by definition, the isohydric pH value represents the pH value of that buffer solution which undergoes no change on coming into contact with soil. This situation can exist only when the pH value of the soil is equal to that of the buffer solution. If the reaction of the soil and that of the buffer are different, some change is bound to take place, resulting in a transfer of the base from one to the other. In short, the isohydric method depends not on a single measurement, but on a series of titrations from which the buffer in which the soil would undergo no change is determined; an absolute measure of the pH value of the soil is thus obtained.

The problem of finding isohydric pH values resolved itself, in the first instance, in the choice of a series of buffer mixtures, the acid-salt proportion of which could be easily ascertained and any change readily detected. Boric acid-borate and acetic acid-acetate mixtures proved useful for the purpose; the former covered the range between pH 7.8 and 10, and the latter between pH 3.7 and 6.

Table 51. Composition of buffer mixtures

Acetate - Acetic acid

pH............................	3.72	4.05	4.27	4.45	4.63
Acetic acid, 0.2 N.... (cc.)	90	80	70	60	50
K- acetate, 0.2 N .... (cc.)	10	20	30	40	50

Boric acid - KCl - KOH

25 cc. of 0.2 N boric acid and 0.2 N KCl mixture
plus cc. of 0.2 N KOH diluted to 100 cc.

pH	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8	10.0
KOH (x)	1.32	2.0	2.95	4.27	6.0	8.2	10.7	13.35	16.0	18.42	20.4	21.95

A mixture of acetate-acetic acid, or of borate-boric acid could be easily analyzed by titrating with standard acid, ana the pH value of any mixture could then be ascertained from the titration curve. In Table 51 (above) are given pH values of K acetate-acetic acid and K borate-boric acid mixtures. These data, when plotted, give smooth curves from which any intermediate value can be interpolated.

Any change in the pH value of these buffers can be measured by titrating before and after shaking with the soil. Since any increase or decrease in the basic portion of the buffer is brought about by a corresponding change in the base content of the soil, and since the pH value of the soil and that of the buffer have been equalized by shaking, the final pH value of the mixture, as determined by titration and interpolation from the curve, gives the pH value of the soil

resulting from a certain change in its base content, which in turn is given by the change in the acid titration value of the buffer on shaking with the soil. Thus by using a series of buffers, a number of values are obtained which represent increasing changes in the base content and the corresponding changes in the pH value of the soil. When plotted, these values give a smooth curve, which may be called the isohydric titration curve of the soil. From this curve is interpolated the pH value of the buffer, which would undergo no change in its titration value. Since at this point the soil obviously would undergo no change in its base content either, this point represents the isohydric pH value of the soil.

For standardizing the working conditions of the method outlined, the following preliminary determinations had to be made:

(a) Effect of time of shaking on the equilibrium between soil and buffer solution.

(b) Effect of soil-buffer ratio.

(c) Fate of the borate ion.

The results of these preliminary experiments showed that equilibrium is attained in two hours, longer shaking up to 48 hours making no appreciable difference; soil-buffer ratios ranging from 1:20 to 1:5 gave practically the same results; and the concentration of the borate ion remained the same before and after shaking of the buffer with the soil.

Detailed Description of the Method. Stock solutions of potassium acetate-acetic acid and potassium borate-boric acid of pH values 4, 5, 6, 8, 9, 1 are made. Two hundred-cc portions of these solutions are shaken for two hours with 10-gram portions of the soil and the suspensions are filtered. The filtrates are titrated with standard acid, methyl orange being used as indicator. For the amount of acid required, the pH value is read from the curve. Assuming that when the state of equilibrium is reached, the soil and the buffer are isohydric with respect to the hydrogen-ion concentration, and assuming that the base lost or gained by the buffer represents a gain or loss by the soil, we know the gain or loss of base by the soil in reaching the isohydric pH value. Thus a series of values corresponding to the series of buffer solutions is obtained, which when plotted give a smooth curve, from which the pH value corresponding to no change in the buffer is interpolated. The acetate-acetic acid buffer evidently cannot be used for calcareous soils. For these, borate-boric acid buffers alone are suitable, and only the upper portion of the curve is obtained. A number of typical isohydric titration curves of soils are given in Figure 63.

It will be seen that most of the soils give a straight-line relationship throughout the entire titration curve. It should be noted that the isohydric titration curve is not expected to be identical with the straightforward titration curve of the soil. It is only at the pH value of the natural soil that the two curves can be expected to coincide. We can of course compute the buffer capacity, the lime requirement,

or the base-exchange capacity of the soil to any pH value from the isohydric titration curves. There is also a much simpler way of drawing the isohydric titration curve, i.e., shaking the soil with various buffers and finding the pH value of the buffer after shaking, and from the titration curve of the buffer computing the value of the base removed from or added to the soil. The fact that these curves are perceptibly straight merely indicates that points of inflection have been suppressed by the high salt concentration of the buffer, and the variations have smoothed out. Just as we found that the pH value of the soil in N KCl is not affected by soil-water ratio, there is no effect of soil-buffer ratio on the course of the isohydric titration curve. Almost all the methods of finding the so-called

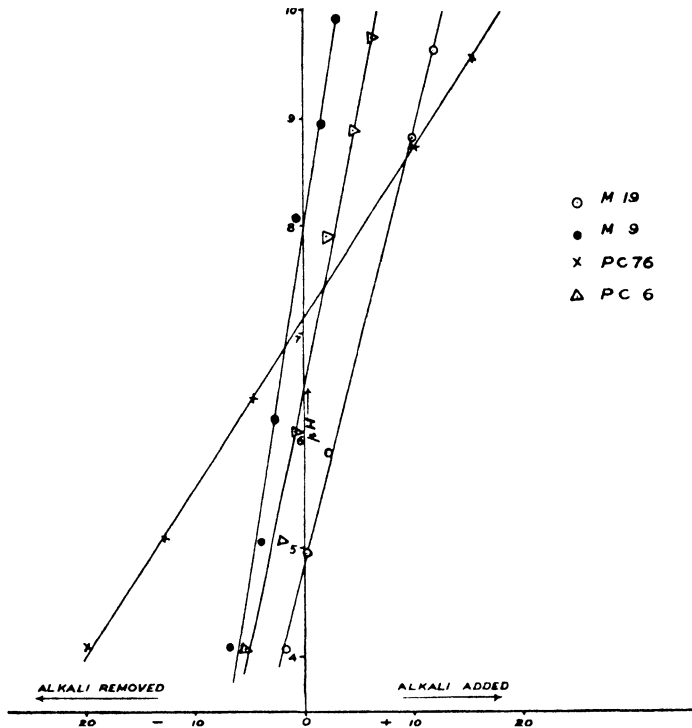



Fig. 63. Isohydric Titration Curves of Soils

base-exchange capacity of soils make use of some salt from which the base is removed by the soil, and the amount thus removed is related to the base-exchange capacity. It would be much better if the technique outlined above is adopted for the purpose, the amount of base taken up by the soil being determined by titration of the buffer or more simply by noting the change in its pH value. Probably two such values would define the whole curve, and its slope would determine the buffer capacity of the soil, which may be defined as milligram equivalents of alkali per 100 grams of soil required to produce a change of 1 unit on the pH scale.

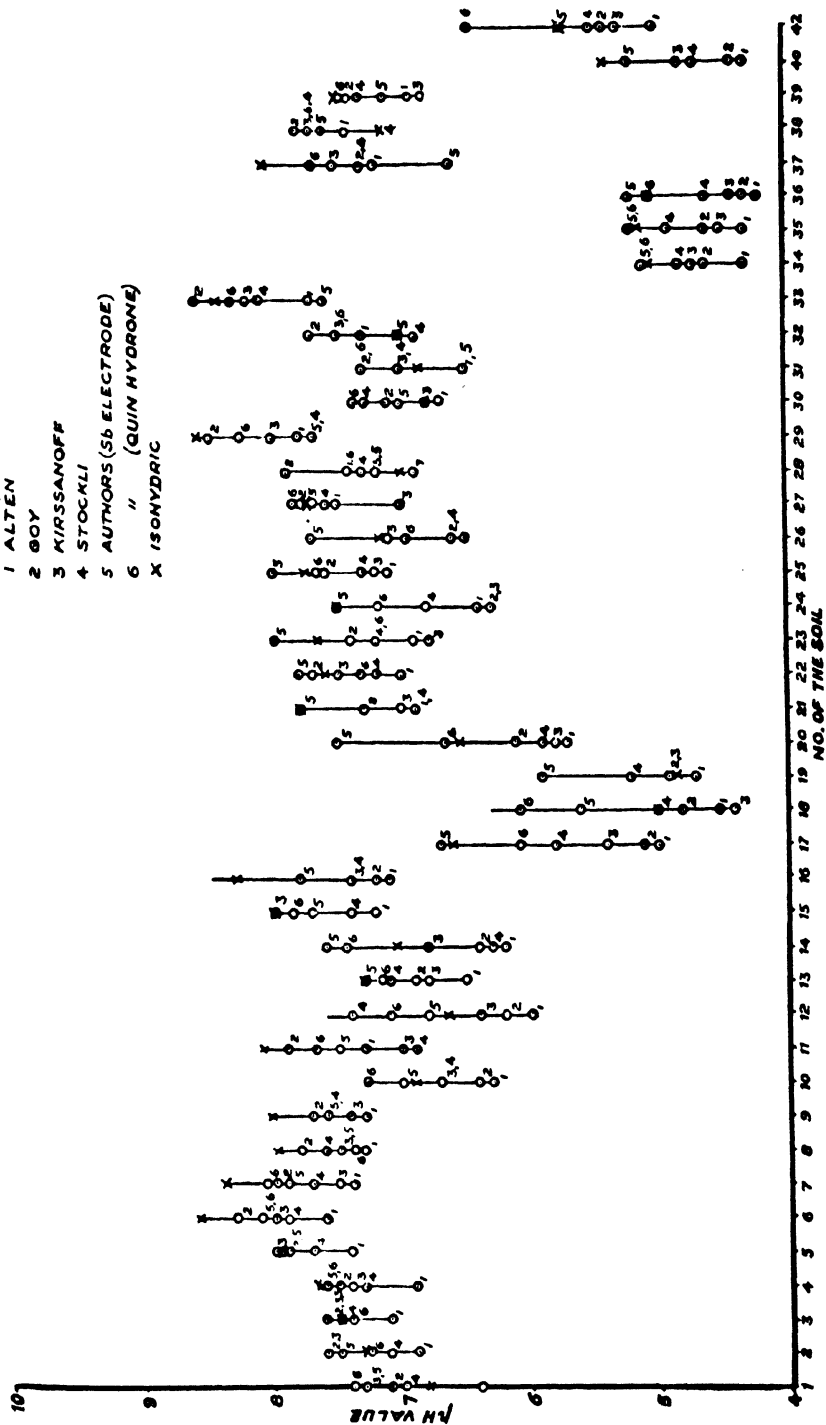



Fig. 64. The pH Values of Soils as Determined by Different Workers and by Different Methods

Comparison with Other Methods. In view of the difficulty of measuring the pH value of soils by the usual methods, the agreement between the soil reaction determined by any of the standard methods and the isohydric pH value can only be approximate. For comparison, the pH values were determined in a soil-water ratio of 1:5, with the antimony electrode and also with the quinhydrone electrode after shaking for one hour. The pH values of these soils had been determined by four other workers. All these values are included in Figure 64 which brings out clearly the wide variations that may be expected in pH measurements by the ordinary electrical methods. The agreement between the isohydric pH values and those determined by the antimony or quinhydrone electrode is better than that between the values determined by other workers. This better agreement is evidently due to the fact that these three sets of values were determined on uniform samples under similar conditions; whereas values determined by other workers were obtained on slightly different samples, possibly under different sets of conditions. The necessity of specifying the conditions of such measurements is, therefore, quite obvious.

It is futile at this stage to argue which method of pH measurement would give values nearest to field conditions. This will depend on what we are looking for. Actual field conditions change from day to day; indeed, there are wide variations of reaction within a few inches. The microbiological population, the proximity of root hairs, the moisture content and a host of other factors would influence the pH value, because we are dealing with a weak electrolyte, the equilibrium conditions of which can be upset by slight changes in the environmental conditions. These variations must be smoothed out if the pH value is to be defined in its relation to the state of neutralization of the soil, and one way of doing so is to determine its isohydric pH value.

pH Value of Highly Alkaline Soils

Highly alkaline soils form a class by themselves. They invariably contain a certain amount of sodium carbonate or bicarbonate, on account of which it is difficult to determine their isohydric pH value by the above method. They are, however, already in equilibrium with a sodium carbonate-bicarbonate buffer solution which determines their pH value. The reaction of such soils can be easily determined by finding the concentration of sodium carbonate-bicarbonate and then interpolating the pH value from the titration curve of NaOH with CO_2. The pH values of various mixtures of carbonate-bicarbonate at different concentrations were determined with the glass electrode, both in water and in 0.1N KCl solution, the latter values being uniformly lower by 0.2 pH than the former. The following relation was found to hold between pH values and the carbonate-

bicarbonate ratio as well as the total concentration of the mixture in 0.1N KCl solution:

$$\text{pH value} = 8.67 + 0.018A - 0.0032B$$

when B = cc of 0.1N alkali (carbonate + bicarbonate) in 100 cc solution

A = per cent of Na_2CO_3 in B.

From this relation the pH value of any alkaline soil is determined by shaking the soil with 0.1N KCl solution, filtering and titrating an aliquot of the filtrate for carbonate-bicarbonate. Since the pH value in KCl is lower than that in water solution by 0.2 pH, this amount is added to the pH value obtained from the formula to correspond to the pH value in water solution.

Table 52. The pH values of alkali soils calculated from carbonate-bicarbonate ratio and determined directly (soil : water ratio, 1:5)

Soil No. P.C.	0.1N Carbonate (cc.)	0.1N bicarbonate (cc.)	pH in water suspension	
			Calc.	Found
57	0.6	0.7	9.70	9.80
58	14.1	9.83	9.85	10.08
59	0	1.0	8.87	8.66
60	36.8	16.4	9.95	9.94

In Table 52 are given pH values of certain typical alkaline soils determined by the electrical method using the antimony electrode, and the values obtained by titrating the 0.1N KCl solution extract for carbonate-bicarbonate. The agreement is sufficiently close to illustrate the general principle involved. It might be pointed out that the method is not applicable unless the amount of sodium carbonate-bicarbonate in the soil is sufficiently large. For soils containing little or no free alkali carbonate-bicarbonate, the usual isohydric method is suitable.

We have discussed several methods of finding the base equivalent of soil acidoids, which carry the soil to the neutralization of the first hydrogen, assuming the soil acidoid to be a dibasic acid. It was pointed out that the pH value at which the second hydrogen is neutralized is in the neighborhood of 10.8, at which point the maximum dispersion of the Na soil is observed. The titration curve in this region, however, is extremely insensitive to pH changes on addition of alkali, and therefore the location of the exact point is difficult, especially as the measurement of pH value in this neighborhood is also liable to error. The formula relating to the pH value of carbonate-bicarbonate mixtures offers a simple method of determining this portion of the curve much more accurately, by shaking the H soil with increasing concentrations of sodium carbonate and finding the concentrations of the carbonate-bicarbonate, which fixes the pH attained by the soil, whereas the amount of bicarbonate determines the amount of alkali taken up by the soil.

CHAPTER XXI

INTERACTION BETWEEN ANIONS AND SOILS

As a general rule we may state that soils will take up from solution only that anion which can form an insoluble salt with one or more soil constituents. We have seen, for instance, that SO_4 ion will be removed quantitatively by a Ba soil, and oxalate and carbonate by a Ca soil. In fact, we could remove any anion from solution by shaking it with a soil containing the appropriate cation. This simple reaction has baffled many workers, especially in the case of phosphates, and the disappearance of nitrites has also been a favorite subject of controversy. We shall deal with these separately.

Removal of Phosphate Ion

Considerable work has been done on the so-called adsorption of phosphates by soil and other constituents usually present in it. A close perusal of the literature on the subject, however, reveals that an important point has been missed by practically every worker on the subject, namely, the pH value of the medium from which the so-called adsorption was supposed to have taken place.

The formation of the phosphates of Al, Fe, Ca and Mg is possible in the soil; but as all these phosphates are extremely sensitive to the concentration of hydrogen ions in the solution, it is needless to resort to the so-called adsorption of phosphates by soils and allied substances, since simple precipitation as an insoluble salt would explain the disappearance of the phosphates. We can, for instance, dissolve or precipitate, partially or wholly, any of these phosphates merely by adjusting the pH value of the solution. However, we shall stick to the conventional methods of study and deal with the removal of the PO_4 ion from solutions of H_3PO_4, KH_2PO_4, K_2HPO_4, K_3PO_4 and Ca $(H_2PO_4)_2$ by gels of alumina, silica, ferric hydroxide and their mixtures, as well as soil acidoid and saloids.

Preparation of Materials

Silica gel was prepared by the addition of 5% HCl to sodium silicate solution of 1.185 density under violent agitation.

Hydroxides of Al and Fe were prepared by precipitating from sulphate and chloride, respectively, with the addition of ammonia.

Silicates of Al and Fe were prepared by mixing normal solutions of the required chlorides of the metals with sodium silicate solutions of equivalent strength.

All these gels were thoroughly washed with distilled water, free of all electrolytes. H soil was prepared by 0.05N HCl treatment and saloids by treatment with hydroxides. Silica and sesquioxides were determined in the various silicates after preparation and various percentages recorded on the air-dry basis. The air-dry moisture was allowed for in every case.

PO_4 was determined by precipitation with ammonium molybdate as $(NH_4)_3\ PO_4 \cdot 12MoO_3 \cdot 2HNO_3 \cdot H_2O$, using large excess of molybdate solution in the presence of concentrated HNO_3. When washed with KNO_3 solution it becomes $(NH_4)_3PO_4 \cdot 12MoO_3$, which can dissolve in excess KOH and be back-titrated against standard HCl. Each cc of normal KOH used is equivalent to 0.003088 gram of P_2O_5. This method was found to be both rapid and accurate.

Five-gram portions of the various air-dried gels were shaken mechanically for four hours (time required for equilibrium condition) with 100-cc solutions of calcium dihydrogen phosphate of different concentrations in narrow-mouth bottles of 200-cc capacity. The mixtures were then allowed to stand overnight, after which an aliquot of the supernatant liquid was pipetted out for analysis. The phosphate and calcium contents of the solutions were estimated before and after shaking and the amounts taken up by the various gels obtained. Calcium was estimated as calcium phosphate gravimetrically. Since the solution contained phosphate ions, all the calcium could be precipitated by the mere addition of ammonia solution. This appeared more convenient than precipitation as oxalate. pH values were determined by a carefully calibrated antimony electrode. The results are summarized in Table 53.

The amount of Ca removed in every case was equivalent to that of the P_2O_5 removed; that column, therefore, has been omitted. It is seen that silica gel does not take up phosphate or Ca ions from the solution. It might be pointed out that in the preparation of silica gel there is need for exercizing great care, as even a small amount of alkali left in it can cause the precipitation of a certain amount of phosphate. This point will be referred to again. Both Fe and Al gels remove Ca and P in almost equivalent amounts, the former removing a smaller quantity. This appears to be due to the formation of calcium, aluminum, or iron phosphate. If the amount of ions removed is plotted against their equilibrium concentrations, straight lines are obtained.

One remarkable thing about these results is that although silica gel itself is completely unreactive toward the solutions of calcium dihydrogen phosphate, its presence increases the reactivity of both alumina and ferric oxide in the silica gels. However, when the proportion of silica is increased beyond a certain limit (gel C) a fall in the reactivity results. The formation of the complex compounds

of Ca, Al, Fe and phosphates is evidently brought about by the electronegative and electropositive residual valences of Al and Fe. The subject requires further study as regards the exact nature of these compounds and the conditions under which they are formed.

The results obtained with various gels do not indicate completion of the reaction, but there is evidence to show that the Ca and phosphate removed tend to be equivalent to the Al or Fe in the solution.

Table 53. Removal of Ca. and P. from calcium dihydrogen phosphate solutions by oxides of Si, Al and Fe; and silicates of Al and Fe

Oxides of Si, Al, Fe						
M. mols. P_2O_5 in original sol.	pH	Silica (m. mols. P. removed)	pH	Al_2O_3 (m. mols. P. removed)	pH	Fe_2O_3 (m. mols. P. removed)
5.5	3.44	0	5.62	2.6	5.14	1.69
4.4	3.60	0	5.77	2.16	5.30	1.42
3.3	3.62	0	6.02	1.66	5.92	1.12
2.19	3.66	0	6.20	1.10	6.18	0.85
1.10	3.82	0	7.10	0.69	6.80	0.61
0.66	3.96	0	7.24	0.585	7.64	0.496
Al silicate gel	A (6 m. mols. Al)		B (5 m. mols. Al)		C (4 m. mols. Al)	
5.5	5.02	4.12	5.55	4.05	5.60	0.832
4.4	5.34	3.40	5.68	3.30	5.80	0.664
3.3	5.76	2.50	5.73	2.40	5.90	0.492
2.19	6.42	1.62	6.24	1.57	5.96	0.391
1.10	7.12	0.83	6.66	0.79	......	....
0.66	7.81	0.53	6.92	0.52	6.40	0.134
Fe silicate gel	A (5.1 m. mols. Fe)		B (3.9 m. mols. Fe)		C (2.95 m. mols. Fe)	
5.5	5.12	3.04	5.42	2.94	5.46	0.600
4.4	5.30	2.30	5.81	2.24	5.48	0.482
3.3	5.86	1.73	6.02	1.66	5.74	0.401
2.19	6.60	1.12	6.10	1.08	6.28	0.282
1.10	7.02	0.59	6.42	0.58	6.52	0.172
0.66	7.64	0.42	6.88	0.42	6.60	0.126

As will be shown presently, this condition is attained in the case of potassium dihydrogen phosphate. In this case also there was no removal of the phosphate ion by silica. The results with Al and Fe silicates are given in Table 54.

It will be seen that increasing amounts of phosphate ions are removed from solutions of increasing concentration, the amount ultimately becoming almost equivalent to the amount of Fe or Al contained in the particular hydrogel; but in no case does it exceed that amount. This shows that the chemical reaction has been carried to completion and that adsorption as such is playing no part whatsoever. The increase in the extent of the reaction is in accordance

with the law of mass action. No subsequent increase beyond the stoichiometric proportion is observed at any concentration.

Similar experiments were then tried with phosphoric acid solutions alone. As before, there was no removal of phosphoric acid by silica. Results for Fe, Al hydrogels and Al silicate are given in Table 55. The amount removed in every case is very small. The

Table 54. Removal of P from KH_2PO_4 solution by silicates of Al and Fe

Al silicate m. mols. of P_2O_5 used	m. mols. of P_2O_5 removed by 5 gms. of silicate (R)					
	A (6 m. mols. of Al)		B (5 m. mols. of Al)		C (4 m. mols. of Al)	
	pH	R	pH	R	pH	R
8.57	6.12	5.59	6.00	5.00	5.56	3.68
7.50	6.08	5.35	6.00	4.82	5.50	3.62
6.43	6.00	5.02	5.78	4.51	5.42	3.56
5.36	5.78	4.40	5.72	4.11	5.38	3.18
2.14	5.64	1.84	5.60	1.70	5.34	1.67
1.07	5.48	0.972	5.52	0.94	5.30	0.91
0.64	5.40	0.634	5.44	0.60	5.30	0.60
Fe Silicate	A (5.1 m. mols. of Fe)		B (3.9 m. mols. of Fe)		C (2.95 m. mols. of Fe)	
8.57	6.92	4.84	7.08	3.60	.....	.....
7.50	6.80	4.83	7.02	3.59	7.18	2.69
6.43	6.74	4.41	6.94	3.50	7.12	2.67
5.36	6.68	4.00	6.80	3.42	7.00	2.59
2.14	6.42	1.62	6.62	1.50	6.80	1.42
1.07	6.34	1.08	6.50	0.82	6.74	0.80
0.64	6.30	0.61	6.44	0.59	6.68	0.57

Table 55. Removal of P from phosphoric acid solutions by oxides of Fe and Al and silicate of Al

m. mols. of P_2O_5 in solution	M. mols. of P. removed (R)					
	Fe_2O_3 (10 m. mols.)		Al_2O_3 (16.7 m. mols.)		Al silicate (6 m. mols. of Al)	
	pH	R	pH	R	pH	R
30.7	2.12	0	2.68	0	2.12	0
15.2	2.46	0.9	2.74	2.60	2.14	0
12.2	2.64	0.62	2.82	7.40	2.14	0
9.2	2.82	8.1	2.96	6.00	2.24	0.3
6.1	3.10	5.7	3.18	5.60	2.32	0.4
3.0	3.42	3.0	3.52	3.00	2.58	1.3

reason for this obviously is the low pH value of the solutions, which prevents the precipitation of the Al and Fe phosphates. It is also evident that with increase in concentration of phosphoric acid solution, when the final pH value follows systematically, the percentage removal of phosphate ions also follows the same order.

Experiments were then conducted in order to find out the exact pH value at which complete precipitation of Fe and Al phosphate can take place. For this purpose aluminum hydroxide gel was mixed with phosphoric acid solution containing 30.7 millimols of P_2O_5 per liter. The volume of acid solution added was slightly in excess of

that required to dissolve the gel completely on mechanical shaking for a couple of hours. To 20-cc portions of this solution increasing volumes of NH_4OH (0.188N) were added, and the amount of aluminum phosphate precipitated was determined in each case. The results are given in Table 56. These data show that when the pH value of the mixture is equal to 3.06, the entire quantity of aluminum phosphate is precipitated. The reaction apparently is extraordinarily sensitive to pH changes.

Table 56. Effect of pH value on the precipitation of Al phosphate

cc. of 0.188N ammonia added	pH	Percentage of Al phosphate precipitated
25	2.5	14.5
30	2.55	28.5
35	2.60	48.5
40	2.66	63.5
45	2.74	75.0
50	2.82	93.0
60	3.06	99.8
80	3.90	100

Table 57. Removal of P from ammonium phosphate by aluminum silicate

m. mols. of P in sol.	m. mols. of P removed by the silicate (R)					
	A (6 m. mols. Al)		B (5 m. mols. of Al)		C (4 m. mols. of Al)	
	pH	R	pH	R	pH	R
30.7	7.10	5.73	7.62	5.08	7.6	3.72
15.2	7.02	5.72	7.34	5.07	7.52	3.71
12.2	6.64	5.70	7.12	5.07	7.44	3.70
9.2	6.60	5.68	7.04	5.06	7.26	3.70
6.1	6.52	4.83	6.80	4.31	7.02	3.60
3.1	6.34	2.58	6.52	2.41	6.82	2.37

The experiments were then repeated with the same four gels by using H_3PO_4-NH_4OH mixtures of pH value slightly over 6. This actually constituted an ammonium phosphate-phosphoric acid buffer. As usual, there was no removal of phosphate ion by silica gel. The results with three silicates containing different amounts of Al are given in Table 57.

P_2O_5 almost equivalent to the amount of Al_2O_3 in the aluminum silicate is precipitated when the pH value is above 3, and the amount of phosphate in solution is sufficient to precipitate all of the aluminum in the aluminum silicate in the case of the co-precipitated silicate prepared in the laboratory. It is necessary to bear this qualification in mind, as one might be led to believe that the sesquioxide in natural soils can be precipitated in this manner. Further light will be thrown on this question later.

We have seen that the removal of phosphates by Fe-Al silicates

can be explained on the basis of well known chemical reactions and there is no reason to assume the existence of adsorption.

A good deal of work on the fixation of phosphates by different types of soils has been done, but the difficulty always has been that sufficient information on the nature of the soil or the pH value of the medium has not been made available, and correct interpretation of the results has, therefore, not been possible. In many cases phenomena that could not be explained as simple chemical reactions involving precipitation were ascribed to adsorption.

Working first with a H soil containing 52% clay, there was absolutely no removal of phosphate from solutions of potassium dihydrogen phosphate. The same was the case with Na and K soils, as would be expected. Ca soil removed from solutions phosphate ion equivalent to the Ca saloid in every case, irrespective of the strength of the phosphate solution as long as it contained enough to cause complete precipitation. Curiously, there was no removal of phosphate by a Mg soil. This was puzzling until it was recalled that the precipitation of Mg phosphate takes place only when ammonia is added in sufficient quantity to make the solution alkaline. This is the well known analytical procedure in estimating phosphates as Mg pyrophosphate. So when sufficient ammonia was added the entire Mg saloid in the soil was converted into Mg phosphate, the removal of which, thus, was equimolecular. By way of illustration results with Ca and Mg soils containing increasing amounts of saloids are given in Table 58.

Table 58. Removal of phosphate ion by Ca and Mg soil

m.e. Ca in the soil	m.e. P_2O_5 removed	m.e. Mg in the soil	m.e. P_2O_5 removed
23.8	24.0	8.33	8.30
35.7	36.1	16.66	16.80
47.6	47.5	24.99	25.10
59.5	60.4	33.32	33.10

The two columns in each case give the m.e. of Ca saloid or Mg saloid in the soil and milliequivalents of P_2O_5 removed when shaken with potassium hydrogen phosphate.

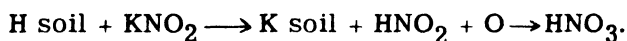
The above results leave no doubt that phosphates are fixed by soils in nature through chemical reactions. If conditions are not favorable for such removal, e.g., if the pH value of the soil is low, or there are no Ca or Mg saloids, or if it does not contain any active Al or Fe oxide, no such fixation can take place. It is hoped that in all future studies of this nature experimenters will first look for some natural explanation based on well known chemical reactions; it is because adsorption was taken for granted that crucial experiments were not devised to track down the exact nature of the reactions involved.

CHAPTER XXII

OXIDATION OF NITRITES AND OXALATES IN SOILS

It is well known that ammonia and ammonium salts formed in soils by the breakdown of nitrogenous organic matter or added in manures are oxidized to nitrites and nitrates before being assimilated by plants. According to the generally accepted view, this process, known as "nitrification" is biological in nature and is effected in two stages by two distinct species of bacteria. This reaction has been described as microbiological, chemical and photochemical by different workers, and evidence has been brought forth and refuted in favor of or against one or the other; the subject has remained highly controversial and lacking in conclusive evidence as to the exact mechanism of the reaction.

Curiously enough this mechanism is extremely simple and appears to have escaped notice because it is obvious. The soil acidoid, on reacting with KNO_2, for instance, is converted into K saloid with the liberation of HNO_2, which is oxidized to HNO_3 as soon as it is formed by the oxygen present in the air:

$$\text{H soil} + KNO_2 \longrightarrow \text{K soil} + HNO_2 + O \rightarrow HNO_3.$$

The nitric acid thus produced reacts with the remaining KNO_2, forming KNO_3 and liberating fresh HNO_2 (which again is oxidized to HNO_3), as well as with the K soil, changing it back into H soil. The regenerated H soil would again react with the remaining KNO_2, liberating fresh HNO_2 and so on, until practically all the KNO_2 is converted into KNO_3. Typical results with a H soil are given in Table 59.

It will be seen that the reaction is complete in about 13 hours and goes on in the dark. It is therefore not photochemical. It is worthy of note that within a brief period of 13 hours, as much as 0.2 gram of KNO_2 is completely oxidized to KNO_3 by only 5 grams of soil. Incidently, no bacterial agency could be expected to bring about such huge conversions under normal conditions; moreover, the soil, being acid-treated, was free from bacteria. To clinch matters, the experiment was repeated with soils kept in chloroform and mercuric chloride, and subjected to sterilization by heating in an autoclave under a pressure of 50 lbs. In no case was the extent of the reaction

affected. These results leave no doubt that biological and photochemical factors play no part whatsoever in the oxidation of nitrites to nitrates by soils.

It might be argued that the experiments have been carried out under conditions which do not exist in the field. The technique of shaking with 100 cc of water was adopted because it lent itself to easy reproducibility. Further tests were made with very much smaller amounts of water under conditions that prevail in nitrifying soil.

Table 59. Oxidation of KNO_2 by H Soil
(0.212 gm. of KNO_2 added to 5 gm. soil and 100 cc. of water)

Time (hours)	KNO_2 oxidized in the dark (gm.)	KNO_2 oxidized in diffused light (gm.)	KNO_3 formed (gm.)
0.5	0.014	0.017	0.020
1.5	0.037	0.047	0.045
2.75	0.072	0.072	0.087
5.5	0.123	0.119	0.148
7.25	0.156	0.152	0.101
9.5	0.170	0.172	0.202
13	0.199	0.206	0.240

Table 60. Oxidation of KNO_2 solution by H soil

0.0559 gm. KNO_2 mixed with 5 gm. soil

Time	KNO_2 oxidized (gm.) water added 2.5 cc.	KNO_2 oxidized (gm.) water added 100 cc.
6 hours	0.0351	0.0120
24 hours	0.0441	0.0146
48 hours	0.0481	0.0160
7 days	0.0559	0.0165

Five-gram portions of a H soil were each mixed with 2.5 cc of water containing 0.0559 gram of KNO_2, and the amount oxidized was determined after different intervals. In another set of experiments the total volume of solution was made to 100 cc by adding 97.5 cc of distilled water, and the amounts of nitrite oxidized after different intervals of time were determined as before. The results given in Table 60 show that oxidation actually proceeds at a much faster rate when the amount of water is small. The enhanced rate is also due to the fact that in the latter case there is free access to air, without which no oxidation is possible.

It is interesting to compare the oxidation of nitrites to nitrates by soil acidoid with that brought about by corresponding amounts of HCl and acetic acid. Accordingly, different weights of a H soil

and equivalent amounts of HCl and CH_3COOH were each kept in contact with 100 cc of nitrite solution containing 0.212 gram of KNO_2, the samples being shaken as usual. The results given in Table 61 show that the amounts oxidized by the soil lie between those oxidized by HCl and by CH_3COOH. Beyond a certain concentration the soil acidoid can oxidize larger amounts than can acetic acid. Further, the amounts oxidized by soil compare rather favorably with those oxidized by HCl. This would appear rather strange in view of the enormous difference in the relative strengths of the two types

Table 61. Oxidation of KNO_2 by equivalent amounts of soil acidoid, CH_3COOH, and HCl

Soil acidoid		CH_3COOH		HCl	
soil added (gm.)	KNO_2 oxidized (gm.)	0.1N acid (cc.)	KNO_2 oxidized (gm.)	0.1N acid (cc.)	KNO_2 oxidized (gm.)
0.1	0.010	2.5	0.012	2.5	0.032
1.0	0.0510	5.0	0.033	5.0	0.095
2.0	0.1259	10.0	0.063	10.0	0.173
3.0	0.1501	15.0	0.089	15.0	0.191
4.0	0.1890	20.0	0.107	20.0	0.194
5.0	0.200	25.0	0.119	25.0	0.199

Table 62. Effect of neutralizing a H soil with increasing amounts of NaOH on the oxidation of KNO_2 (0.212 gm. of KNO_2 added to 5 gm. of soil)

NaOH added 0.1N sol. cc.	pH after shaking with NaOH	KNO_2 oxidized (gm.)
0	3.5	0.1954
5	4.5	0.1021
10	5.36	0.0424
20	5.72	0.001
30	6.44	0
40	7.32	0
50	8.72	0

of acids. It must be remembered, however, that the reaction is of a continuous nature and does not depend on the strength as much as on the quantity of acid present; that is why increasing quantities of acidoid as well as of soluble acids oxidize larger quantities of nitrites in the given time, namely 13 hours.

Since the oxidation of nitrites is brought about by soil acidoid, its neutralization must lead to decrease or complete inhibition of this reaction. This is shown in Table 62. It will be seen that the amount of nitrite oxidized decreases with gradual neutralization of the acidoid with NaOH. When the pH value has reached 5.7 no oxidation is observed in 13 hours.

It was observed, however, that the limit of pH 5.7 is only applicable to 13 hours' shaking. When tests are made after long intervals of

time, H soils neutralized to pH values above 8, as well as natural soils having pH values between 8 and 9, do show appreciable oxidation. This will be clear from Table 63, in which these results are recorded.

A careful examination of these results will show that since higher pH value indicates only a reduction in the quantity of acidity, the major effect is a slowing down of the rate of oxidation. It is clear that in nature the residual acidity of ordinary agricultural soil would be quite sufficient to bring about the conversion of nitrites into nitrates. It should also be remembered that in natural soils, even under highly alkaline conditions, the pH value is low in the immediate neighborhood of root hairs because of CO_2 production. Though it is true that at higher pH value, the rate of conversion slows down considerably, there is no doubt that it does take place.

Table 63. Oxidation of KNO_2 by soils having pH values higher than 7
(Amount of KNO_2 added: 0.212 gm.)

H soil neutralized with	pH value	KNO_2 oxidized (gm.)	
		after 30 days	after 50 days
NaOH	7.32	0.0108	0.0195
NaOH	8.72	0	0.0151
$Ca(OH)_2$	7.1	0.0116	0.0182
$Ca(OH)_2$	8.4	0	0.0141
Natural soils			
P.C. 13	8.5	0.020	....
P.C. 123	8.0	0.042	....
P.C. 155	8.9	0.035	....
Blank KNO_2 sol.	8.4	0	....

When, however, the soil acidoid is completely neutralized by treatment with alkali equivalent to the total acidoid, it loses its oxidizing capacity entirely. The results obtained with two completely neutralized soils after being shaken with nitrite solutions for one month showed no oxidation of nitrites. These results also offer another logical explanation of the decreased productivity of highly alkaline soils. It is obvious that excessive alkalinity might lead to the complete inhibition of nitrate formation.

As different H soils have different amounts of acidoid in them, it is evident that the amounts of nitrites oxidized in a given time by equal weights of different soils will be different. The results would be somewhat similar to those obtained when different weights of the same soil or different quantities of a soluble acid are taken. To study this aspect, a number of H soils differing in acidoid content were selected and compared for their oxidizing power as before. Results with only a few typical soils are given by way of illustration in Table 64.

These results show conclusively that it is the quantity of acidoid in the soil which is responsible for determining the rate of oxidation of nitrites into nitrates. The correlation coefficient between

acidoid equivalent of the soil and the amount of nitrite oxidized was worked out for 46 soils and was found to be 0.83, which is highly significant. Further evidence on this point was obtained by determining the oxidizing capacity of a H soil after being heated to various temperatures. As shown previously, there is very little change in the acidic properties of soils up to a temperature of

Table 64. Oxidation of KNO_3 with different H soils
(0.212 gm. of KNO_2 added to 5 gm. soil)

Soil No. P.C.	pH	Acidoid (m.e./100 gm.)	KNO_2 oxidized (gm.)
13	3.5	58.0	.2060
68	4.5	5.6	.0086
70	4.2	14.0	.0285
110	4.9	18.0	.1899
142	3.7	43.0	.2060
173	4.8	22.0	.0776
262	6.1	6.0	.0120
133	4.5	4.7	0
Sand	6.9	0	0

Table 65. Oxidation of KNO_3 by H soil heated to different temperatures.
(0.212 gm. of KNO_2 added to 5 gm. of soil)

Temperature (^{o}C)	KNO_2 oxidized in 13 hours (gm.)
29	0.210
100	.206
200	.206
300	.207
400	.172
500	.042
600	.021
770	.020

$400^{o}C$, above which this property decreases progressively. In conformity with other properties of the soil as a weak electrolyte, there is no decrease in the oxidizing property up to $400^{o}C$, above which there is a steady decrease in the amount of nitrite oxidized. This will be clear from Table 65.

Oxidation of Oxalates

Oxalates have very little importance in soil economy. A study of their reaction with soil is interesting because it throws light on the chemistry of the reactions involved. The quantitative precipitation of Ca in Ca soil as oxalate by an equivalent amount of K

oxalate has already been dealt with. This is a rapid reaction which is completed within 10 to 15 minutes. This, however, is followed by a slow reaction which continues for several days. It is the nature of this slow reaction which we shall consider in this section. A convenient method of following up these reactions would be the measurement of pH values at regular intervals of time. In the first instance, when soil saloids are gradually neutralized with oxalic acid we get a back-titration curve. Now if any oxalic acid disappears afterward, the titration curve should undergo a shift toward higher pH values. This is actually found to be the case, as will be seen from Figures 65 and 66 for Na and Ca soils.

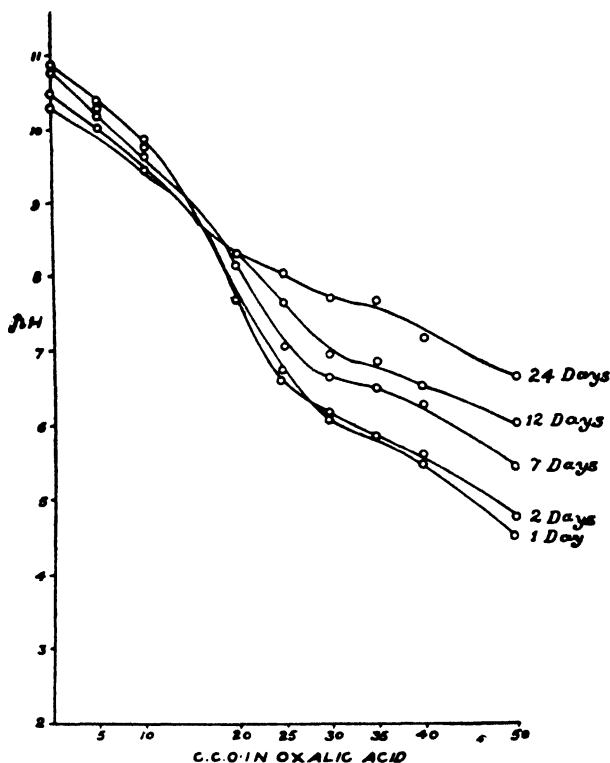



Fig. 65. Reaction of Oxalic Acid with Na Soil

The results with ammonium and magnesium soils were similar. It is remarkable that this slow rise is the greatest in the case of Ca soil. This was at first ascribed to the extremely fine state of subdivision of the freshly precipitated Ca oxalate, but it was found that there was practically no difference in the course of reaction whether Ca oxalate was freshly precipitated on the soil or directly added to it in the solid state. It is, however, true that the amount of Ca oxalate decomposed in a given time increases with the amount added. The decomposition of an insoluble substance (Ca oxalate) by another insoluble substance (a H soil) with increase in

pH value and formation of yet another insoluble substance (Ca saloid) is one of the most fascinating reactions in soil chemistry.

A number of H soils were examined in a similar manner. Five milliequivalents of $Ca(OH)_2$ were added to 10 grams of the soil. This was followed by the addition of an equivalent amount of oxalic acid, resulting in the complete precipitation of Ca oxalate on the soil surface. The soils were shaken in a mechanical shaker for about one month; pH values were determined at certain intervals. At the end of this period Ca saloid was determined by the K carbonate-acetate-oxalate method described previously. The results

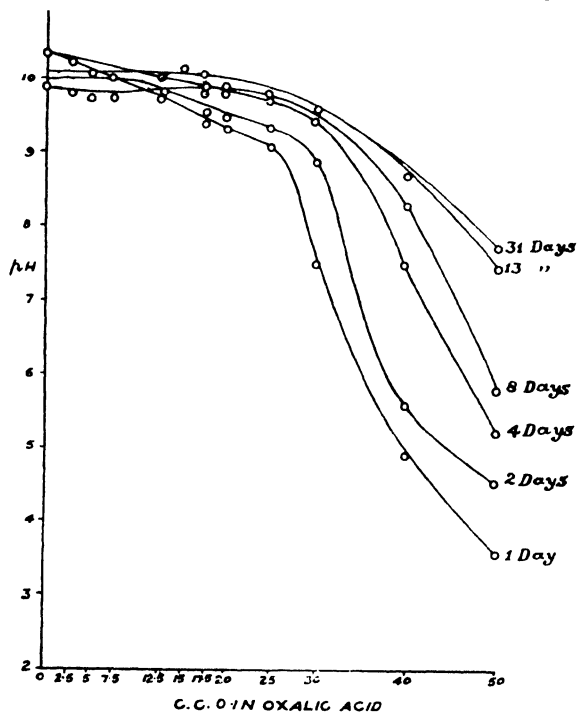



Fig. 66. Reaction of Oxalic Acid with Ca Soil

of a few typical soils of a larger collection are given by way of illustration in Table 66, which indicate that the power of decomposing Ca oxalate varies with different soils.

The slow disappearance of the oxalate ion with the formation of free $Ca(OH)_2$ and the consequent rise in pH value may be due to two causes:

(1) Formation of Fe or Al oxalates which may be even more insoluble than Ca oxalate.

(2) Oxidation of the oxalate ion with the production of CO_2.

The first possibility is rendered unlikely by the fact that several Fe and Al hydroxides and silicates were prepared, but not one of them gave any indication of forming insoluble precipitates with

oxalates, which could be reasonably considered identical to those produced in the case of soils. In fact, Ca oxalate is the least soluble of all the oxalates and its decomposition with the formation of more insoluble oxalates could not be supposed to occur. The second possibility, i.e., oxidation of the oxalate ion by the soil, was explored by estimating the total oxalate ion in the soil at the end of the reaction. This was done by adding to the suspension a known volume of normal HCl solution, and filtering and titrating an aliquot of the filtrate with standard permanganate, after neutralizing with NaOH and acidifying with H_2SO_4. Preliminary experiments had shown that all the Ca oxalate in the soil could be determined in this way. The decrease in the amount of oxalate ion over the amount originally added of course gave the quantity oxidized by the soil. These values are included in Table 66. Very large amounts

Table 66. pH and time reaction of H soils with Ca oxalate

Soil No.	Ca saloid (m.e.)	pH values after days (0)	(1)	(7)	(10)	(17)	(24)	(30)	Ca oxalate oxidized (m.e.)	Mn (m.e.)
1	0.36	3.09	4.67	4.96	5.25	6.18	6.44	6.56	0	0.1
7	0.28	2.35	4.74	4.76	4.76	5.20	5.20	5.20	0.40	2.1
13	1.70	2.30	3.27	3.60	3.65	4.00	4.09	4.51	5.40	2.0
15	0.26	2.82	5.26	5.10	5.70	6.55	6.57	6.57	0.36	0.4
32	1.80	2.42	3.56	3.74	4.35	5.53	5.96	6.05	4.80	0.05

of oxalates can be oxidized by some soils. These results are of importance for they bring into prominence the slow oxidizing properties of soils. If oxalates can be oxidized there is no reason why ammonia may not be.

It would be of interest to know if the slow oxidation of oxalates by soils could be hastened by heating the suspension. Boiling the suspension under reflux for varying lengths of time showed no evidence of accelerating this remarkable property.

In a search for the cause of this property the manganese content of the soils was determined; but as will be seen from Table 66, there is no correlation between the Mn in the soil and its oxidizing property. The reaction is neither influenced by the amount of acidoid in the soil, nor by its state of neutralization, except that when the pH value is too high oxidation is affected adversely.

From all this it is obvious that soil acidity, as such, has nothing to do with the oxidation of oxalates. As the reaction likewise cannot be ascribed to any microbiological factor, because soils were found to retain their oxidizing property intact even when sterilized, it remained only to test the various main constituents of the soil, namely, SiO_2, Al_2O_3, and Fe_2O_3.

To 2-gram portions of each of these oxides, 5 m.e. of potassium oxalate was added and the amounts decomposed were determined after one week. The results given in Table 67 show that considerable amounts of oxalates were oxidized. Similar experiments with ferroaluminum silicates of different composition showed oxidation of oxalates to varying degrees within a week.

Table 67. Decomposition of K oxalate by different oxides and by ferro-aluminosilicates
(50 cc. 0.1N potassium oxalate added to 2 gm.)

Oxide	K oxalate decomposed (cc.)	Oxide	K oxalate decomposed (cc.)
Al_2O_3	10.0	Cr_2O_3	2.9
Fe_2O_3	6.2	CuO	6.1
SiO_2	12.1	PbO	1.4
BaO	6.2	MnO_2	30.8
CaO	5.0	ZnO	1.1

Per cent composition of ferroaluminosilicate			Ratio: $SiO_2 : Fe_2O_3 + Al_2O_3$	K oxalate decomposed after shaking for 15 days
Fe_2O_3	Al_2O_3	SiO_2		
19.3	2.7	55.7	2.53	20.2
11.2	6.3	57.2	3.25	28.4
3.3	13.9	71.2	4.14	35.2
0.6	16.4	73.4	4.31	43.4

These results should leave no doubt that the cause of decomposition of oxalates by soils lies in the very nature of the soil composition, all the three main constituents acting as oxidizing agents. Whether these oxides act as mere catalysts or themselves take part in chemical reactions is a point on which no opinion can be expressed at present.

CHAPTER XXIII

PHYSICOCHEMICAL PROPERTIES OF FERROALUMINOSILICATES AS ALLIED TO SOILS

The chemistry of ferroaluminosilicates is wrapped in obscurity. The complex nature of the compounds involved, the surplus residual valences, and the looseness of the chemical bonds leave us uncertain as to whether we are dealing with chemical compounds or mere mixtures. Alumina is a weak base and silica is a weak acid; both are insoluble in water. Their natural attraction or chemical affinity for each other is so weak, and the reaction products so insoluble that one is not sure whether the resulting mixture is a chemical compound or a solid solution.

There is little doubt that in clay we are dealing with ferroaluminosilicates and that the free acidoid (SiO_2) valences partly occupy the basic valences of aluminum and iron, leaving their acidic characteristics free to accentuate the acidoid characteristic of the SiO_2. These acidic properties may be further intensified in the presence of humic acid in natural soils.

Curiously enough, no serious attempt has so far been made to study exhaustively the various physicochemical properties of silicates prepared in the laboratory, and to show that the simplest iron and aluminum silicates do exhibit all the essential properties characteristic of the natural clays present in soils. A study of these properties has not only emphasized the fact that the analogy is not merely superficial but fundamental, but also has offered a logical explanation of the essential difference between the two.

As a prelude to the study of the various physicochemical properties, we shall in the first instance examine potentiometrically the formation of Fe-Al silicates.

Alumina is a weak base and silica a weak acid; if they are combined with a strong acid and a strong base, respectively, the resulting compounds, as a result of considerable hydrolysis, will behave like an acid in one case and a base in the other. Thus aluminum chloride could be titrated against NaOH just like HCl, and sodium silicate with HCl just like NaOH. Similarly these two compounds could be titrated against each other, just as conveniently as HCl and NaOH, chlorine and sodium leaving their partners as readily

as if they were free. The alumina and silica thus left free, combine with each other and remain suspended in the colloidal state, or come down as an insoluble precipitate. In order to understand the formation of Fe-Al silicates at different pH values, we must refer to Figure 67, which gives the titration curves illustrating the formation of various silicates. Fifty cc of the 0.1N acid or alkali solution was taken and increasing amounts of 0.1N alkali or acid added. The total volume in every case was made up to 100 cc before taking the pH value with the glass electrode.

Titration Curves of Al-Fe Hydroxides and Silicates

For the purpose of this study silicic acid was prepared by adding 7 cc of N HCl to 5 cc of N Na_2SiO_3. Similarly, Al silicate and Fe silicates were formed by the addition of 7 cc of N $AlCl_3$ or $FeCl_3$ to 5 cc of N Na_2SiO_3. The two precipitates were mixed in equivalent amounts and titrated together with NaOH as well as separately. The results are plotted in Figure 68. It will be seen that the titration curves of mixtures of Al and Fe hydroxides and silicic acid are not identical with those of the Fe and Al silicates. The latter behave like stronger acidoids than the former.

We have seen that silicic acid or Al and Fe silicates can be precipitated by addition of HCl or chlorides of Al or Fe, respectively, to sodium silicate. By varying the proportions of HCl and the Al-Fe chloride, precipitates of varying proportions of Si, Al and Fe can be prepared. These precipitates were titrated with NaOH, both as such and after drying. The results are plotted in Figures 69, 70 and 71.

The essential difference between the titration curves of Fe and Al silicates should be noted. In the former there is no well-defined point of inflection, which is fairly prominent in the latter. On the whole, Fe gives weaker acid residue than Al. Another point worthy of note is the effect of drying, which has reduced the acidoid content very considerably.

The titration curves of a number of H soils are compared to those of silicates in Figure 72. The striking similarity of the soil titration curves to those of silicates is well brought out and should leave no doubt that in soils we are dealing with similar compounds: the curves of one or another of various silicates could be fitted almost exactly to those of some soil. The variations in soils, therefore, could be satisfactorily accounted for by the variations in the silica sesquioxide ratios of the silicates, as well as by the nature and amount of the sesquioxides.

In H soils we have an initial pH value which varies from 3.5 to 6.5, whereas in dry ferroaluminosilicates the variation is from 5.3 to 6.2. This difference is satisfactorily accounted for by the presence of humic acid in soils. This view is confirmed by determining the titration curve of a soil from which humus has been removed by alkali extraction and comparing it with that of the original soil which

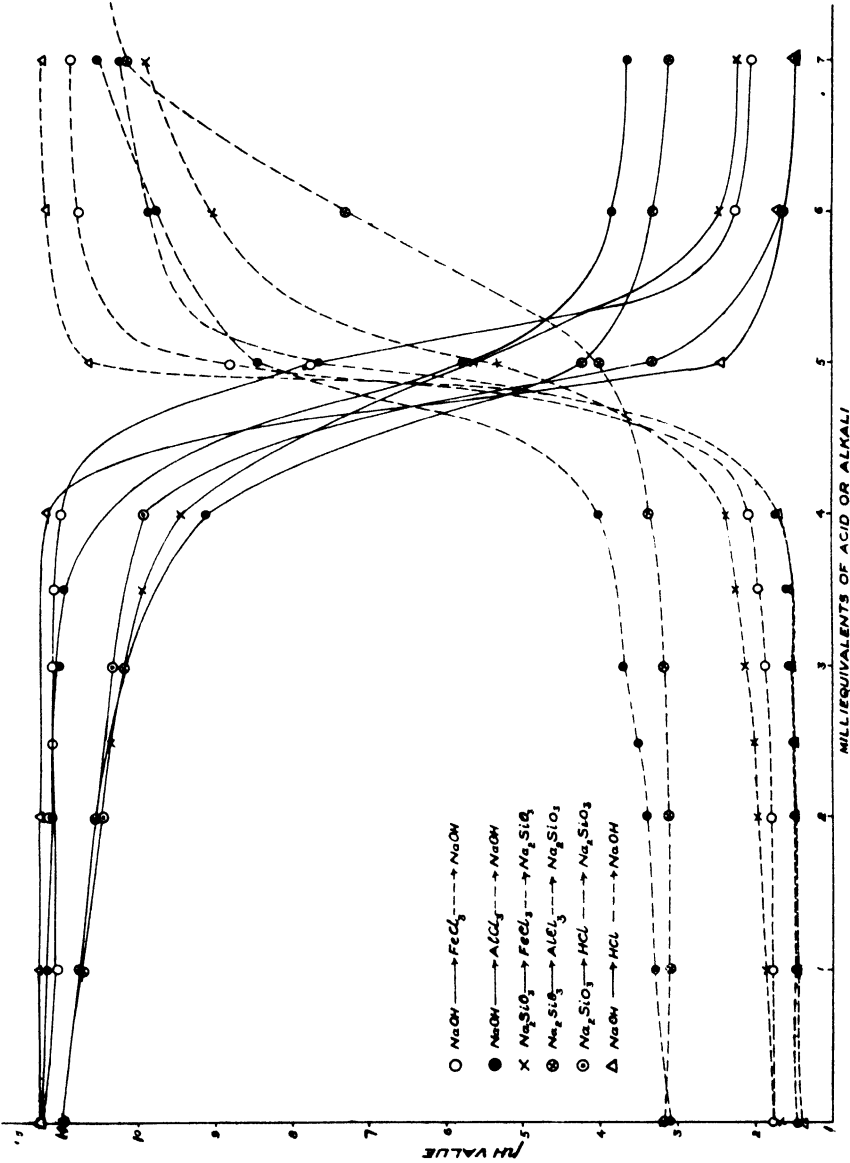



Fig. 67. Filtration of Na_2SiO_3 and NaOH with HCl, Fe Cl_3 and Al Cl_3

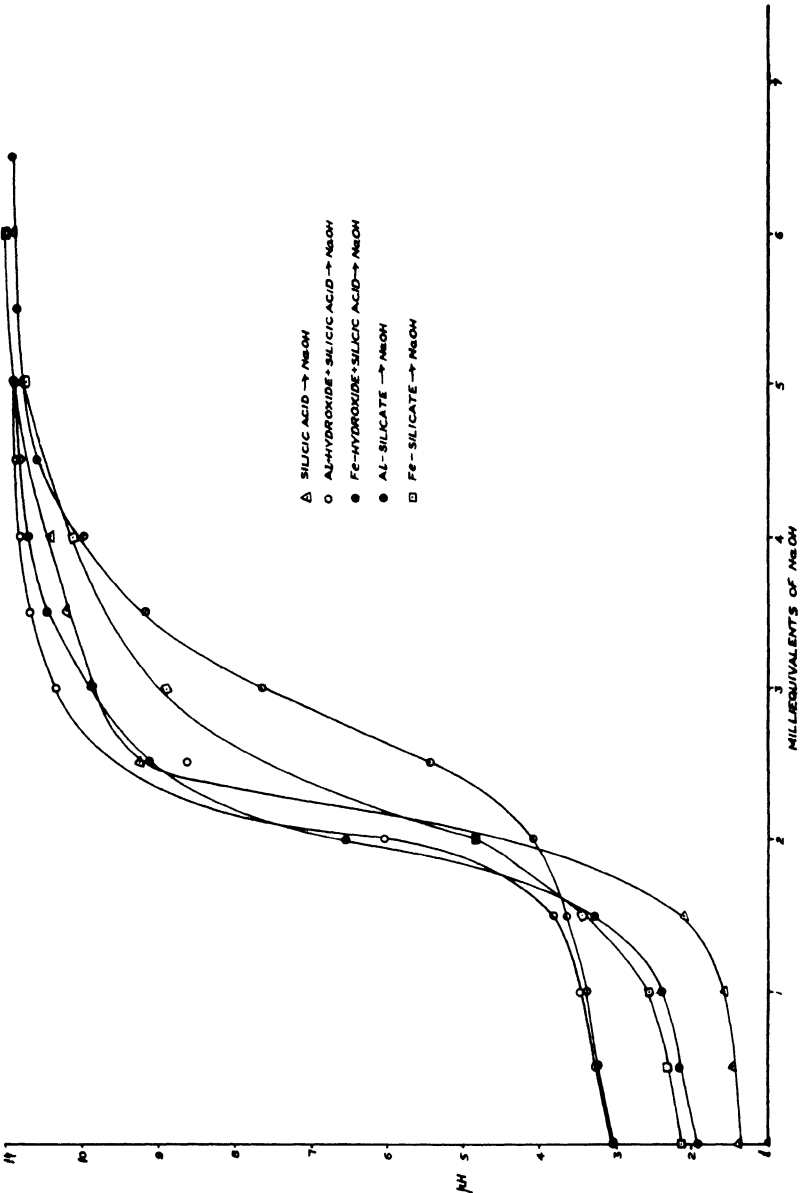



Fig. 68. Titration Curves of Fe and Al Silicates and Mixture of Al and Fe Hydroxides and Silicic Acid

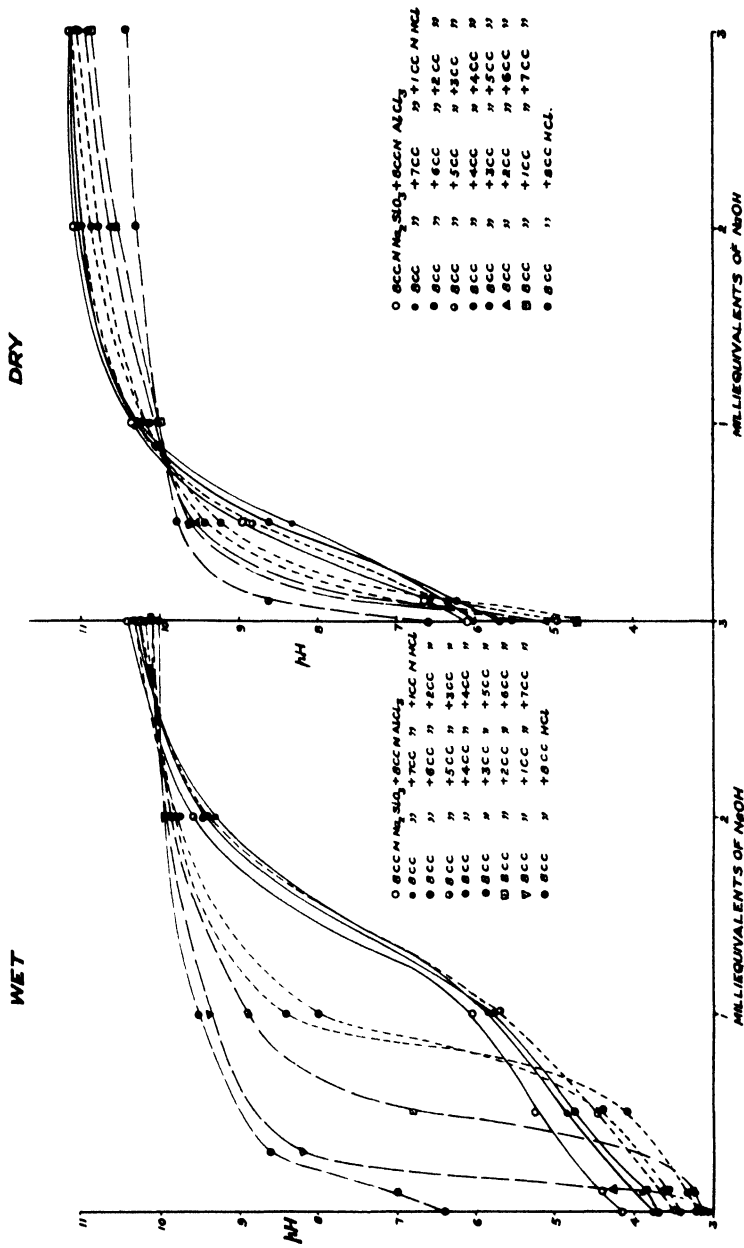



Fig. 69. Titration Curves of Al Silicates

Fig. 70. Titration Curves of Fe Silicates

Fig. 71. Titration Curves of Ferroaluminosilicates

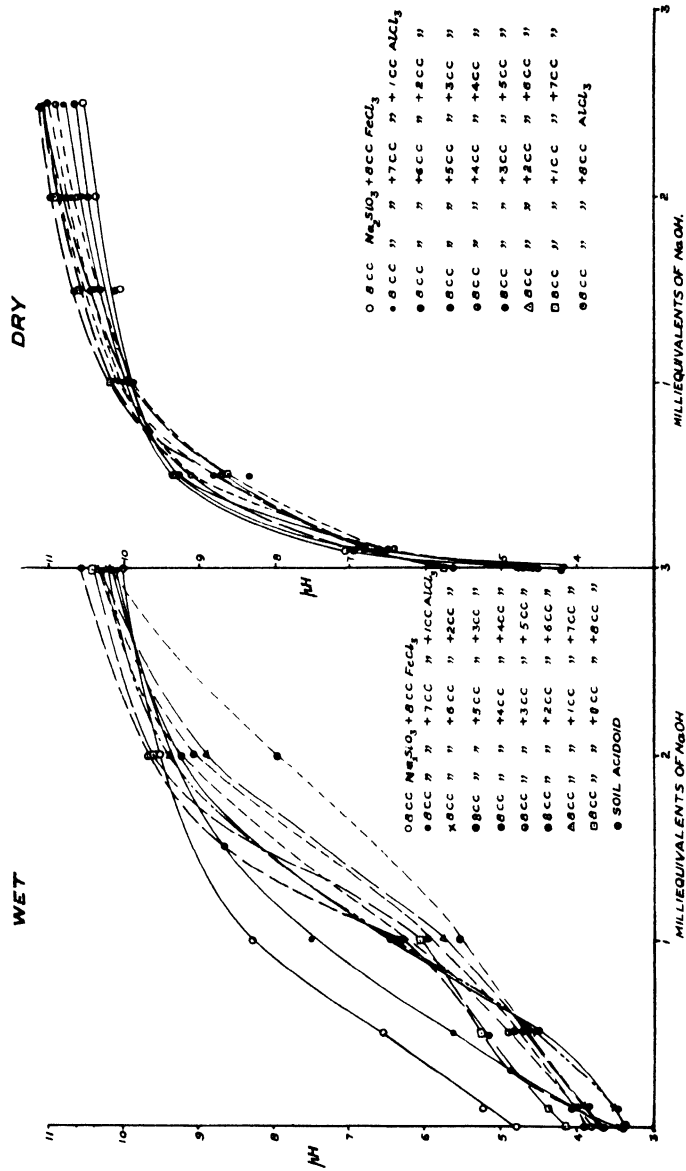



Fig. 72. Titration Curves of Ferroaluminosilicates and Soils

contained 4.32% humus and also after adding humic acid to the extracted soil (Figure 73). It will be seen that the initial pH value rises considerably on the removal of humus and lies within the range of ferroaluminosilicates. The pH value again drops when humus is replaced.

The infinite varieties of ferroaluminosilicates which can form in nature must render fruitless any attempt at classifying them on the basis of their chemical composition. However, all these compounds and their mixtures show the properties of weak electrolytes and behave as acidoids, when free from bases. The exact composition of

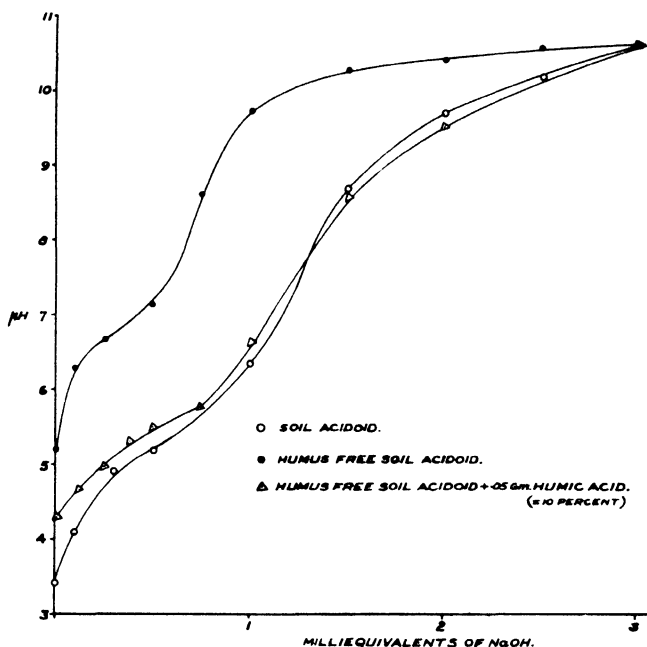



Fig. 73. Effect of Humus on the Titration Curve of Soil Acidoid

the clay complex is not important, and is not reducible to any laws. It has been produced by forces that can be classified only in a general way, and no two soils in the world are exactly alike. We are, therefore, only concerned with the "quantity" and the "intensity" of the acidoid in a soil. The simplest conception of this residual acidity is the analogy with ferroaluminosilicates, the titration curves of which are identical with those for soils.

Interaction Between Ferroaluminosilicates and $CaCO_3$, Ammonia, and Sulphides

For this study, mixtures of varying silica, alumina and ferric oxide contents were prepared either by mixing the freshly precipi-

tated and dried constituents together or by their simultaneous precipitation from the same solution. Silica, alumina and ferric oxide were prepared in the following manner:

Silica was obtained by mixing with continuous stirring a hot solution of HCl containing 10 per cent by weight of the gas with an equal volume of sodium silicate solution of density 1.85. The mixture set to a gel in about an hour's time. It was then broken into small lumps and washed free from salts, etc., and allowed to dry slowly at room temperature. The dried lumps were ground.

Alumina was obtained as a gelatinous precipitate by the slow addition of ammonium hydroxide, with vigorous stirring, to a solution of aluminum sulphate at room temperature. The precipitate was washed free from salts and ultimately dried in an air oven at 90-

Table 68. Interaction between silica, alumina, ferric oxide and silicates and calcium carbonate

Substance	pH	CO_2 liberated (m.e./100 gm.)		Base equivalent (NH_3) (m.e./100 gm.)
		Before heating	After heating	
Silica	6.66	10.1	8.62	2.4
Fe_2O_3	7.82	13.8	11.9	0
$SiO_2 + Fe_2O_3$, 1:1	7.22	10.7	31.7	17.5
Al_2O_3	7.68	12.4	10.6	8.25
$SiO_2 + Al_2O_3$, 1:1	6.68	8.51	51.61	17.5
$SiO_2 + Al_2O_3 + Fe_2O_3$, 1:1:1	6.95	5.50	57.25	....
$SiO_2:Fe_2O_3$, 3.87:1 (Coprecipitation)	7.58	17.04	83.04	....
$SiO_2 + Al_2O_3$, 1.65:1 (Coprecipitation)	......	18.84	98.66	....

100°C for 12 hours. Ferric hydroxide was precipitated from its chloride solution in a similar manner. It was subsequently washed and dried.

It will be noted that the various gels were prepared in as simple a manner as possible. It is useless to take any elaborate precautions in their preparation or purification. The extent of the chemical reactions in all these substances depends on their active mass, which in turn depends on such a variety of factors that it would be impossible to reproduce the results except by chance. These variations clinch the argument that similar variations in soils are rather a reflection of the basic similarity of the substances responsible for them.

The decomposition of $CaCO_3$ by these substances as well as interaction with ammonia was studied in the usual way. The results given in Table 68 show that both these reactions proceed normally as in the case of soil.

Two points are of interest: that mixtures in each case bring about greater decomposition of the carbonate than the individual constituents, and that when the two are coprecipitated the chemical

reaction is much more vigorous than when they are precipitated separately and mixed. This point will be elaborated later.

The interaction between soils and sulphide has been shown to be a straightforward decomposition of the sulphide with formation of H_2S, the quantity of which is equivalent to the basic portion of the sulphide reacting with the soil, which again equals the base equivalent of the soil acidoid.

Silica was prepared by mixing slowly with continuous stirring equimolecular solutions of HCl and sodium silicate. The mixture was allowed to set to a gel which was washed free of salts with distilled water and allowed to dry slowly. The decomposition of BaS was studied at different stages of drying: every time a sample was taken for treating with sulphide, a representative portion was dried at 100 to 110°C for moisture content.

The results (Table 69) bring out the striking effect of moisture content on the decomposition of sulphide. A portion of the gel was shaken with excess $Ba(OH)_2$ solution at the same time. The amount

Table 69. Reaction of silica and alumina with BaS and $Ba(OH)_2$

Silica			Alumina		
moisture (%)	H_2S evolved (m.e./gm.)	$Ba(OH)_2$ neutralized (m.e./gm.)	moisture (%)	H_2S evolved (m.e./gm.)	$Ba(OH)_2$ neutralized (m.e./gm.)
1000	23.8	26.3	2270	23.37	33.56
920	23.6	26.2	1500	23.18	29.1
890	22.8	26.0	1230	20.80	27.0
690	19.5	21.6	1060	19.32	25.6
490	17.9	20.8	150	4.75	10.8
233	4.3	......	50	4.35	5.4
20	4.1	5.9	......	......	......

of $Ba(OH)_2$ neutralized by each sample is also included in the table. The two sets of values are almost identical, thus establishing the essential similarity of the two reactions, namely, decomposition of BaS and neutralization of $Ba(OH)_2$.

Alumina was prepared by a process somewhat similar to the one described for silica. To a normal solution of aluminum sulphate an equivalent amount of ammonia solution was added with vigorous shaking. The resulting gel was washed free of salts with distilled water. Reaction with BaS and $Ba(OH)_2$ was studied exactly as in the case of silica. The results (Table 70) show the close similarity of silica and alumina in this respect.

Iron oxide prepared in a similar way turned out to be poor in this respect. Even at 2000% moisture content it could decompose only 2.7 milliequivalents of sulphide.

Attention was next directed to aluminum silicate, which was also prepared in a similar way by the addition of aluminum sulphate to sodium silicate with vigorous stirring. Two samples of the silicates were prepared with different SiO_2/Al_2O_3 ratios:

Sample No. 1. $SiO_2:Al_2O_3 = 2.8:1$
Sample No. 2. $SiO_2:Al_2O_3 = 1:2.01$

Results of decomposition of BaS (Table 70) show the general similarity of behavior with silica and alumina. There does not appear to be much difference in the two silicates due to the variations in the SiO_2/Al_2O_3 ratio, although the results for silicate No. 2 are slightly higher than those for No. 1.

Ferric silicate prepared similarly by the addition of 2N solution of ferric chloride to an equivalent amount of sodium silicate showed values for BaS decomposition that were distinctly lower than those for aluminum silicate. This will be seen from Table 71. There

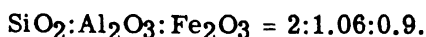
Table 70. Reaction of aluminum silicate with BaS

Sample No. 1		Sample No. 2	
Moisture (%)	H_2S evolved (m.e./gm.)	Moisture (%)	H_2S evolved (m.e./gm.)
3232	31.02	1540	38.28
2600	30.70	1050	23.52
1232	30.36	670	19.20
950	21.73	233	9.24
698	18.37	107	7.80
300	8.40	43	7.84
143	7.75		
43	7.56		

Table 71. Reaction of ferroaluminosilicate and ferric silicate with BaS

Ferroaluminosilicate		Ferric silicate (SiO_2:Fe_2O_3 = 2.6:1)	
Moisture (%)	H_2S (m.e./gm.)	Moisture (%)	H_2S (m.e./gm.)
1376	19.8	1150	21.7
921	17.6	730	16.6
802	17.1	320	9.96
497	13.6	210	8.06
200	9.9	66	8.25
134	8.0	21	8.11
77	7.3		
9	7.0		

was not much improvement when aluminum was introduced in the ferric silicate, with a mixture of ferric chloride and aluminum sulphate. The ratio of the various ingredients in the ferroaluminosilicate was:

$$SiO_2:Al_2O_3:Fe_2O_3 = 2:1.06:0.9.$$

To complete the analogy between soil acidoid and ferroaluminosilicates, the hydrolysis of ethyl acetate as well as free acid produced on shaking with KCl were determined with a number of silicates. The chemical composition of the silicates is given in Table 72.

The hydrolysis of ethyl acetate was studied with the mixtures of ferroaluminosilicates by mixing 5-gram portions with 25 cc of 5 per cent ethyl acetate solution. The suspensions were kept at 50°C for 4 hours, during which they were shaken by hand at frequent intervals. After this they were cooled and filtered and an aliquot was titrated against standard alkali. The quantities of acetic acid produced in the case of various silicates are given in Table 72. The values increase in the order of increasing ratio of silica and alumina in the mixtures. The amount of HCl produced on reaction with a neutral salt also follows the same trend.

Table 72. Hydrolysis of ethyl acetate and "exchange acidity" with KCl of ferroaluminosilicates

No.	Fe_2O_3 (%)	Al_2O_3 (%)	Si_2O (%)	Silica/sesquioxide ratio	E (m.e.)	HCl	
						A (m.e.)	B (m.e.)
1	19.3	0	55.7	2.89	1.0	13.0	8.0
2	13.7	3.2	55.5	3.28	1.46	17.0	10.0
3	11.3	6.3	57.2	3.25	1.76	21.0	15.0
4	9.7	8.3	58.4	3.25	1.83	22.0	17.0
5	9.5	8.7	59.8	3.28	1.98	.....	.....
6	9.4	9.6	62.5	3.29	2.70	26.0	20.5
7	5.4	11.3	66.3	3.97	2.80	29.0	23.5
8	3.3	13.9	71.2	4.14	3.32	33.5	26.0
9	0	15.4	76.0	4.97	3.26	34.0	27.1

E = acetic acid produced by hydrolysis of ethyl acetate.
A = "Exchange acidity" by titration to phenolphthalein.
B = "Exchange acidity" by titration to methyl orange.
Note: the difference between 100 per cent and the total constituents of each mixture is due to water of hydration.

Mechanical analysis of ferroaluminosilicates and their moisture absorption from atmospheres of various humidities will be discussed under appropriate sections. All these physicochemical properties of silicates show a close resemblance to soil colloids in all essential respects. We can, therefore, say that soils are nothing but ferroaluminosilicates produced in nature's laboratory.

This assertion opens up a question of general interest, namely, what exactly is the nature of the combination between silica and sesquioxides? We have seen, for instance, that the reactivity of silica is greatly enhanced by the presence of alumina. It is, therefore, of great importance to know how this increase in reactivity is brought about. At the same time we would like to know if the nature of the forces that bind the two molecules is the same in soils as in artificially prepared silicates. It is to be remembered that the manner of formation of the silicates in natural soils is entirely different from that of the laboratory. In nature this combination was brought about by fusion. The compact solid mass thus produced disintegrated due to weathering and thus exposed surfaces which had

monomolecular layers of the silicates. On the other hand, in the laboratory the product has been synthesized by precipitation.

On the face of it one would expect that the fusion would result in molecular combination, whereas precipitation would cause a combination that may be described as amolecular. For instance, as silica and sesquioxides are precipitated, the molecules are sure to form aggregates, and it is these aggregates which mesh together, no doubt by chemical valence forces, but much feebler in intensity. Moreover, the chemical reactivity and physicochemical properties of the silicates must be capable of infinite variations due to chance aggregation influenced by temperature, concentration and state of agitation of the liquids. The artificial silicates, therefore, have a porous structure, whereas individual particles in soils have a compact mass.

This may sound heretical, for the porosity of soils is notorious. However, if we believe that soils have been produced from solid, compact rocks by disintegration, we have to stop somewhere, even if it is the core of the original rock in the heart of the particles. This core is absent in ferroaluminosilicates prepared in the laboratory by precipitation, and this fact constitutes the difference between the two. Not that such a difference is important, except that one will have a greater percentage of active mass than the other; qualitatively, the two would be exactly alike as regards their chemical reactions toward alkalies, and so on. However, when they are subjected to some drastic treatment, such as reaction with a strong acid, obviously their behavior will be totally different. In that case the artificially prepared, porous, amolecular compound of silica and sesquioxides would readily part company with the hydroxides and the acid will "get them", leaving behind some gaps of varying dimensions. Soils on the other hand would resist such treatment. The aluminum and iron forming the monomolecular surface may have their other end strongly attached to the rigid surface of the core that was the original rock. This molecular combination will not allow the acid to dissolve the hydroxides, leaving the silica behind. A portion of it may still dissolve, of course, but only a small fraction as compared to the total amount present; the case of the precipitation of phosphoric acid as phosphate of Fe or Al is similar. In artificial silicates all the Fe and Al will be precipitated, whereas in the case of soils only that portion will be precipitated which constitutes the surface. If this portion is removed by acid treatment prior to the addition of a phosphate, no phosphoric acid is removed.

We shall first study the interaction between silica and weak insoluble bases and then the effect of acid treatment on the physicochemical properties of soils and aluminosilicates. Pure samples of silica, alumina, ferric oxide and magnesium oxide were prepared in the ordinary way by precipitation. They were allowed to dry slowly at room temperature. The dried lumps were ground. Mixing was brought about by (1) grinding (2) shaking (3) boiling and (4) coprecipitation.

Several silica-sesquioxide mixtures were obtained by grinding the constituents together in different molecular proportions for half an hour in a colloid mill, which consisted of a mechanically driven agate pestle and mortar. Their neutralization with ammonia was determined by keeping 5-gram portions of the substance in contact with excess of 0.1N ammonia solution for 48 hours with occasional shaking. The suspension was then boiled to half its volume when excess was driven off, and the amount retained by the substance determined by heating with lime and passing the ammonia in a known volume of standard H_2SO_4. The results obtained with different silica-alumina mixtures as well as the pure constituents before and after grinding are given in Table 73.

Table 73. Neutralization of ammonia by silica, alumina and silicates, determined by two methods

Molecular ratio Silica:Alumina	Ammonia taken up (m.e./100 gm.)			
	Method I		Method II	
	without grinding	with grinding	without grinding	with grinding
1:0	1.2	2.4	10.0	......
0:1	8.2	10.0	10.0	......
1:1	17.5	......	17.5	35.0
2:1	25.0	20.0	30.0	40.0
3:1	25.0	17.5	27.5	30.0
4:1	12.5	25.0	......	......
5:1	10.0	20.0	35.0	45.0

Grinding as such does not appear to affect the reactivity of either alumina or silica; therefore, the increased values of ammonia taken up by the mixtures must be attributed to causes other than grinding. In fact, when the proportions of the constituents are roughly the same, grinding has a slightly adverse effect. It is only when one of the constituents is present in large excess that grinding is effective for a uniform and thorough blending of the two. The significant conclusion brought about by these observations is that intermixing of silica and alumina results in increasing appreciably the reactivity of the material toward ammonia, which persists even when the SiO_2/Al_2O_3 ratio increases to 5:1. It is a remarkable fact that silica and alumina, both practically inert toward ammonia, acquire considerable reactivity when mixed, and that the neutralization value of silica rises from almost nothing to about 20 m.e./100 grams when mixed with a small quantity of alumina.

The technique employed for the study of neutralization by ammonia involved boiling the mixture to drive off excess ammonia. It is possible that thorough mixing of the constituents might have been brought about at that time. In order to find out whether silica can manifest increased reactivity toward ammonia in the mere presence of alumina, i.e., even when silica and alumina are not thoroughly mixed by grinding, the neutralization with ammonia was studied in another way.

Five-gram portions of the various substances were kept over N ammonia solution in a vacuum desiccator for four days and then over concentrated H_2SO_4 for the same interval of time, after which the ammonia retained was determined in the usual way. The results are included in Table 73. These values are somewhat higher than those obtained in the previous case. The effect of grinding is also more significant, resulting in a higher value in every case. The differences between the reactivities of the constituents and the mixtures are again brought out. The reactivity is increased appreciably, even when the constituents are not ground but only mixed thoroughly; but grinding, as is to be expected, increases this value still further on account of better uniformity in the various mixtures.

Similar results were obtained with mixtures of silica and ferric oxide and silica and magnesium oxide (Table 74).

Table 74. Neutralization of silica, ferric oxide, magnesia and their mixtures by ammonia

mol. ratio silica:base	Ammonia taken up (m.e./100 gm.)			
	Silica + ferric oxide		Silica + magnesia	
	without grinding	with grinding	without grinding	with grinding
1:0	1.2	2.4	1.2	2.4
0:1	0	0	0	0
1:1	12.9	17.5	12.5	17.5
2:1	6.25	6.25	9.37	9.37
3:1	9.37	9.37	9.37	6.25
4:1	9.37	11.25	12.5	12.5
5:1	9.37	6.25	9.37	6.25

Table 75. Decomposition of $CaCO_3$ by silica, alumina and their mixtures on grinding

Mol. ratio silica:sesquioxide	CO_2 liberated (m.e./100 gm.)	
	Ferric oxide	Aluminum oxide
1:0	20.1	20.1
0:1	25.7	20.6
0.2:1	......	44.8
0.5:1	......	51.3
1:1	42.4	60.1
2:1	49.6	60.0
3:1	35.3	64.3
4:1	32.5	57.0
5:1	32.4	58.1
6:1	25.1	45.8

Next the decomposition of $CaCO_3$ by the various mixtures and the individual constituents was determined. The method consisted in adding 5 grams of the mixture to 1 gram of solid $CaCO_3$ and about 100 cc of water, heating the suspension and collecting the CO_2 liberated in standard $Ba(OH)_2$ solution (Table 75).

The mixtures in all cases show greater acidity than the constituents.

Boiling or shaking the constituents in the form of suspensions also resulted in enhanced reactivity, as would be expected.

Precipitation of Mixtures by Coprecipitation. Silica and alumina, as well as silica and ferric oxide, were coprecipitated in different molecular proportions by adding calculated amounts of $AlCl_3$ and HCl (or $FeCl_3$ and HCl) solutions to sodium silicate. Ammonia neutralization was determined in the usual way. Besides this their reactivity toward $Ba(OH)_2$ was determined. This was done in two ways. The first was by electrometric titration curves with the antimony electrode, typical examples of which are shown in Figures 74 and 75. In the second method, the $Ba(OH)_2$ uptake was determined by adding 2-gram portions of the materials to 50 cc 0.1N $Ba(OH)_2$ solution, shaking for 15 minutes and then titrating an aliquot of the clear solution. It need hardly be mentioned that 15 minutes' shaking is not adequate for the completion of the reaction, but our immediate concern being the study of the influence of one constituent on the other, only comparative values were desired.

The results of these observations in the case of silica-alumina mixtures are given in Table 76. The neutralization values of the mixtures were read from the titration curves at the points of inflection.

Table 76. Reactivity of silica - alumina mixtures prepared by coprecipitation

Ratio SiO_2/Al_2O_3	Base taken up (m.e./100 gm.)		
	Ammonia	$Ba(OH)_2$ (A)	$Ba(OH)_2$ (B)
0.579	160	120	157
1.235	140	.....	433
3.37	170	.....	400
4.53	190	176	400
8.20	165	118	530
9.47	180	180	520
Pure silica	1.2	.....	.....
Pure alumina	8.2	.....	.....

A = Interpolated from titration curve.
B = $Ba(OH)_2$ removed from excess in solution.

These results show enormous increase in the neutralization values in the mixtures. Besides, when these results are compared to those obtained by mechanical mixing by grinding, boiling or shaking, it is seen that the process of coprecipitation yields mixtures of much higher reactivity. Results with ferric oxide and

zinc oxide were similar; in both cases increased reactivity toward ammonia was recorded, as will be clear from Table 77.

Table 77. Reactivity of ferric oxide-silica and zinc oxide-silica mixtures prepared by coprecipitation

Composition SiO_2/Fe_2O_3	Ammonia (m.e./100 gm.)	Composition SiO_2/ZnO	Ammonia (m.e./100 gm.)
0.164	10	0.18	0
0.523	5	0.80	15
2.42	35	1.57	10
3.87	35	2.82	25
6.45	20	11.14	30
9.16	35	12.76	30
10.00	15		
11.06	10		
Pure silica	1.2		
Pure Fe_2O_3	0		

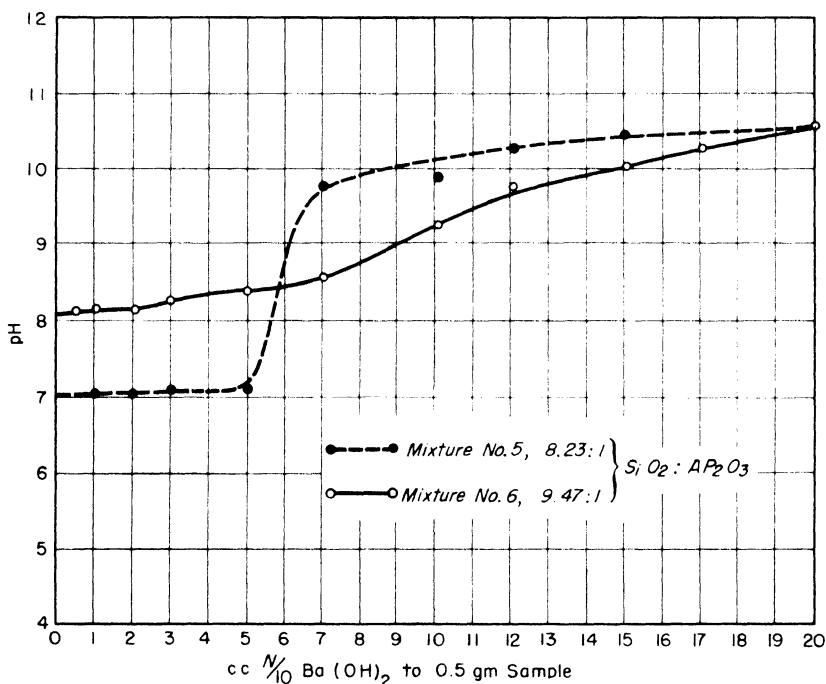



Fig. 74. Titration Curves of Silica-Alumina Mixtures Obtained by Coprecipitation

The interaction between solid silica and insoluble oxides accords with the view that the surface of every solid is chemically reactive. The aggregation of molecules merely results in rendering chemically ineffective those molecules that do not constitute the surface. A

solid in bulk is chemically inert because the mass of the molecules constituting the surface is infinitesimally small. We have already recognized as the active mass of a solid that proportion which constitutes the surface, and we have seen that as regards chemical reactions it is in no way different from matter in the molecular state. Therefore, if the molecules of silica and sesquioxides by virtue of their chemical valence can combine with each other, there is no reason why they should not do so when surfaces constituting the molecules come into contact. Exactly how the enhancement of the chemical reactivity takes place is not very clear, but this much is certain: the effect manifests itself only in the case of dried samples. For instance, the maximum stoichiometric amount of $Ba(OH)_2$ taken up by molecularly dispersed silica or alumina when both have 100% active mass is never exceeded. It is only on drying, when aggregation takes place and the active mass is reduced correspondingly, that differences in their reactivity appear. It is very likely that the combination of silica and sesquioxides results primarily in a change in the intensity of acidity and incidentally in the

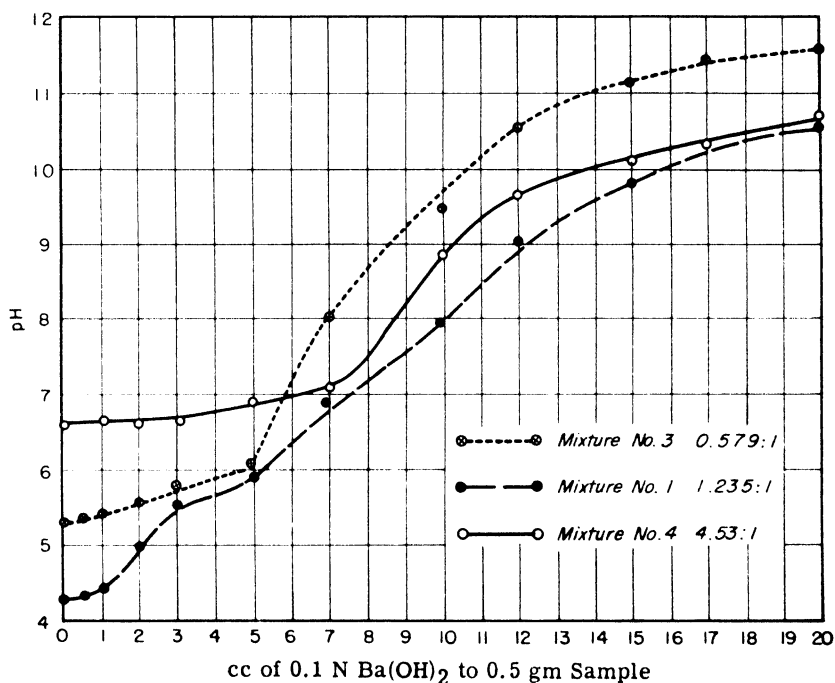



Fig. 75. Titration Curves of Alumina-Silica Mixtures Obtained by Coprecipitation

quantity of acidity, on account of the resulting differences in the size distribution of the aggregates on which the total surface depends.

As pointed out before, in natural soils we have molecular association between silica and sesquioxides and in similar silicates prepared in the laboratory we have associations between aggregates of

molecules. It is necessary at this stage to guard against a possible misconception that is likely to arise from the above statement. When silica or alumina is precipitated separately, the flocculant mass is a molecular dispersion which may consist of strings of monomolecules, plates or even tubes. Therefore, although they may have 100% active mass as regards interaction with a substance in molecular dispersion, interaction between two such conglomerates of molecules will not be a molecular combination in the same sense. Although the surfaces are there, the points of contact are fewer, and therefore the chemical reaction will be restricted to those molecules that can come within the molecular range of attraction. This being the fundamental difference between natural silicates in soils and artificial ones prepared in the laboratory, we should expect a marked difference in the behavior of the two toward acids.

In the present work the dissolving action of acid solutions of varying concentrations on some aluminosilicates as well as on a few typical soils was determined, and its effect on some physicochemical properties of residual material was studied in detail.

Table 78. Removal of sesquioxides from soils and Al silicates by acid.

Strength of HCl	Grams of sesquioxide removed per 100 gm. of dry material								
	Silicates						Soils		
	(1)	(2)	(3)	(4)	(5)	(6)	P.C. 6	P.C. 13	P.C. 123
0.05N	2.37	0.66	0.95	1.12	0.82	0.66	.025	.58	.227
0.1N	7.25	2.60	2.00	2.07	1.15	1.24	.063	.888	.20
0.2N	6.45	3.70	4.10	4.75	1.67	2.32	.094	1.45	.90
0.5N	19.90	12.60	12.50	12.95	6.50	7.85	.194	2.75	1.85
N	34.30	25.40	23.50	21.90	10.75	11.55	.150	2.65	2.95

Six aluminosilicates of the following SiO_2/Al_2O_3 ratio prepared by coprecipitation were used for this study: (1) 0.579, (2) 1.235, (3) 3.37, (4) 4.53, (5) 8.2, (6) 9.47. Similarly the action of these acid solutions was determined on three typical soils: Lab. No. P.C. 6, 13 and 123. They contained 28.4, 55.0 and 85.6% of conventional clay, respectively. They were converted into H soils by 0.05N HCl treatment to bring them to a uniform basis.

Forty-gram portions of each material were leached separately with 500 cc in 100-cc lots of N/20, N/10, N/5, N/2 and N HCl solutions. The amount of sesquioxide leached out in every case was determined (Table 78).

The following conclusions may be drawn from the observation: (1) Soils can resist the action of acid solutions of even moderate strength, such as N HCl, to a much greater extent than aluminosilicates, which in fact tend to lose almost the entire amount of alumina in most cases. (2) The difference in the amounts of the sesquioxides washed out in the two cases (aluminum silicate and soils) goes on increasing with increase in the strength of the acid solution. The results indicate that the association between silica and sesquioxides in natural soils is molecular, whereas in the case

of artificial silicates it is between molecular aggregates. It is of course understood that forces involved in both cases are due to chemical valence.

It would be interesting to see how far the chemical reactivity is affected by the gradual removal of the sesquioxides in the two cases. Neutralization of the residual material by ammonia as well as by $Ba(OH)_2$ after acid treatment of soil as well as aluminosilicates was determined as a measure of their chemical reactivity (Table 79). The amounts of sesquioxides removed by acid treatment were given in the previous table.

Table 79. Effect of acid treatment on the chemical reactivity of soils and aluminum silicates

Strength of HCl	m.e. of ammonia or $Ba(OH)_2$ neutralized per 100 gm.									
	(1)		(2)		(3)		(4)		(5)	
	A	B	A	B	A	B	A	B	A	B
Control	160	157	140	....	170	400	190	400	165	530
0.05N	142	137	.....	....	177	320	115	360	165	500
0.1N	160	157	120	....	165	343	105	380	155	520
0.2N	130	....	140	....	185	360	90	380	125	480
0.5N	....	....	130	....	160	380	62	500	70	600
N	110	....	200	....	92	540	35	640	20	700
	(6)		P.C. 6		P.C. 13		P.C. 123			
	A	B	A	B	A	B	A	B		
Control	180	520	10	20	42	120	22.5	80		
0.05N	165	570	10	10	55	138	22.5	100		
0.1N	165	540	5	20	50	136	22.5	80		
0.2N	145	544	10	20	52	140	22.5	120		
0.5N	70	620	10	20	55	140	27.5	100		
N	30	740	15	20	50	145	27.5	130		

The results with soils do not show any marked variations in their reactivity as a result of acid treatment. In the case of P.C. 13 acid-treated soil, some increase in ammonia as well as $Ba(OH)_2$ uptake is noticed as a result of 0.05N HCl treatment, but thereafter the values remain more or less unchanged, even on more drastic acid treatment and elimination of comparatively larger amounts of sesquioxides. This increase is very probably due to the removal of some residual bases which might have escaped the first acid treatment. This soil (P.C. 13) contains a large amount of Ca saloid which is rather difficult to remove from an undispersed soil. Since there is no subsequent increase in the value of ammonia or $Ba(OH)_2$ taken up, it may be inferred that acid treatment, as such, does not affect the reactivity of soil toward alkalies.

Results with aluminosilicates show that the values of ammonia taken up are not affected appreciably by the gradual removal of alumina until the proportion of alumina becomes very small—in

fact, almost nil. On the other hand, there is absolutely no decrease in the neutralization value for $Ba(OH)_2$ which if anything shows an increase on the removal of alumina. These results again confirm the view that the presence of alumina or iron oxide tends to intensify the acidity without affecting its quantity. Both ammonia uptake and decomposition of $CaCO_3$ are affected by the intensity of acidity, at least in the case of the first hydrogen of the dibasic acidoid. It is in fact somewhat similar to the effect of one ion on another in a binary mixture in changing its dissociation; and as surfaces are as susceptible to such influences as molecules in solution, it is not difficult to visualize the influence of an ampholytoid like alumina on an acidoid. This view is confirmed by the fact that only a small amount of one is required to produce an appreciable effect, and further amounts have very little effect. The removal of alumina or ferric oxide from a silicate would hardly affect the extent of the surface; if anything, a small increase might be expected. Since it is the extent of the surface that determines the active mass or quantity of acidity, we have a slightly enhanced value for the $Ba(OH)_2$ taken up. Soils, on the other hand, only give up the portion of the sesquioxide on the surface. This slightly increases the extent of the surface, but at the same time leaves sufficient so as not to affect the intensity of acidity. For when the sesquioxides form an integral part of the surface in molecular combination with silica, it is difficult to conceive of their complete removal by mere acid treatment.

It is emphasized, however, that beyond this quantitative difference which lies in the very nature of things, the aluminosilicates constituting the soil surface are in no way different from silicates prepared in the laboratory. We have at present no means of reproducing the results achieved by nature; for although we can fuse silica and alumina together, we cannot bring about its disintegration into smaller particles which nature has taken several centuries to accomplish.

The results of acid treatment discussed in the foregoing have indicated the structural differences between natural and artificial silicates. However, by controlling the pH value of the acid solution we can bring out the essential similarity between the two. This can be done by studying the interaction between soils as well as artificially prepared ferroaluminosilicates and acid solutions of different H ion concentration. It is quite obvious that in the breakdown of the silicates with the dissolution of sesquioxides, pH value must play an important role.

The three soils previously used (P.C. 13, 123 and 292) were employed in this case also, and were converted into H soils by prolonged acid treatment. The three silicates used were iron, aluminum and a coprecipitated mixture of the two. The chemical composition of the soils as well as the silicates is given in Table 80. The buffer solutions of different pH values were prepared by mixing N sodium acetate solution with N HCl in requisite proportions. The

Table 80. Composition of H soils and silicates

Substance	Percentages of various constituents			
	Fe_2O_3	Al_2O_3	SiO_2	Water
Soil P.C. 13	19.1	25.6	48.8	6.5
" " 123	22.6	16.4	52.4	8.6
" " 292	16.8	20.4	55.8	7.0
Fe silicate	13.5	......	58.05	28.05
Al silicate	......	13.65	61.6	25.15
Fe-Al silicate	6.15	13.75	47.15	33.25

pH values of these buffer solutions were checked by the glass electrode and the values actually determined are given.

Reaction with Soils. Two-gram portions of the various soils were added to 80 cc of the buffer solutions of different pH values contained in 200-cc bottles. The contents were shaken in a mechanical shaker. After different intervals of time one bottle of each sample in contact with each of the buffer solutions was withdrawn, filtered, and analyzed for iron and aluminum by the usual methods. The results obtained in the case of all the soils were essentially similar; those for P.C. 13 soils are plotted in Figure 76 as typical of the lot.

The following conclusions may be drawn from these results: (1) Ferric oxide is dissolved more readily than alumina by acid solutions, on account of the stronger basicity of the former. (2) The reaction appears to be continuous in the initial stages, the breakdown of the silicate increasing with time; but after 32 hours further increase in the amount of ferric oxide passing in solution is very small, and there is indication that after about 32 hours some sort of constant value might be obtained. In the case of alumina the end of dissolution is reached much earlier. (3) With the rise in the pH value of the acid solutions employed, the amount of sesquioxide passing in solution goes on decreasing. The relationship between the pH value of the buffer solution and the amount of sesquioxide dissolved by it after 48 hours is shown in Figure 77. Maximum amounts are seen to have been dissolved at the lowest pH value. When the pH value increases from 1.04 to 1.85 the fall in the amount of sesquioxides which pass into solution is very great, but with subsequent rise in pH value, further decrease in this quantity is small and slow. (4) The resistance of soils toward acid solutions is well brought out. For instance although P.C. 13 soil contains over 19% of Fe_2O_3 and over 25% of alumina, only 15.7% of the total Fe_2O_3 and 4.89% of the total alumina present in the soil is dissolved. (5) The breakdown of the soil silicates under similar conditions of experiment does not take place to the same extent in all soils. This would obviously depend on the specific surface, which is different in different soils.

Reaction with Silicates. Similar experiments were made with the various silicates. The results in the case of ferroaluminosilicate

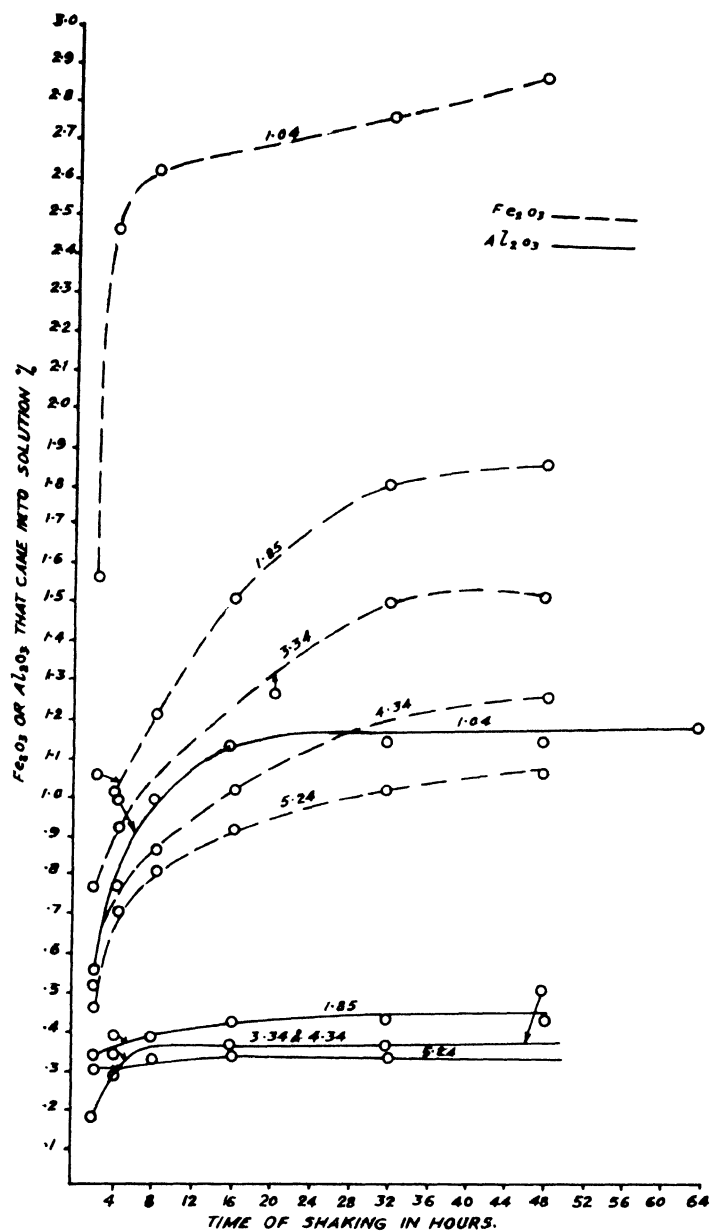



Fig. 76. Interaction between Soil No. P.C. 13 A.T. and Acid Solutions when Shaken Together for Different Intervals of Time

are plotted in Figure 75 and show a general similarity with soils. Results with other silicates showed no fundamental difference and therefore are omitted. The maximum amounts of the sesquioxides dissolved in 100 cc of the various buffer solutions in four hours'

Fig. 77. Interaction of Soils and Ferroaluminosilicates with 80 cc of Acid Solutions of Different pH Values When Shaken for 48 Hours

Fig. 78. Interaction of Soils and Ferroaluminosilicates with 100 cc of Acid Solutions of Different pH Values When Shaken for 4 Hours

time in the case of soils as well as ferroaluminosilicates are plotted against the pH values of the buffer solutions in Figure 78. They bring out the remarkable similarity between soils and artificial silicates; the extent of the reaction in the case of silicates is much larger than with soils, when the pH value of the buffer is 1.04. With other buffer solutions, however, the amounts of sesquioxides passing in solution from silicates are of the same order as in the case of soils. This emphasizes the essential similarity between the two. A gentle treatment only touches both superficially; a more drastic treatment attacks the sesquioxides lodged in the minute capillaries, which also explains the slowness of the reaction. As pointed out before, coprecipitated silicates are molecular compounds of aggregates which would necessarily leave large gaps in the interstices. The dissolution action of the acid on the sesquioxides would amount to interaction in these minute capillary spaces where the rate of reaction must be limited by the rate of diffusion in them.

CHAPTER XXIV

HUMUS IN SOILS

Humus in soils is a complex body, the exact nature of which depends on its origin and mode of formation. It has, however, certain specific properties which distinguish it from other natural bodies, and from the practical point of view the term "humus in soil" is well understood in a general way.

The alkali-soluble humus in soils constitutes a group of substances that are distinct from the rest of the organic matter. The most important common property of this group is that its members, like soil acidoid, exhibit acidic properties and their alkali salts are highly dispersed in water. In this respect the properties of humic acid are so similar to those of H soils that a mixture behaves like a single substance. The so-called humus in soils, therefore, would not require separate treatment; as weak electrolytes they constitute a part of the soil which is in no way different from the rest of the mineral portion.

It is not sufficiently recognized that when we speak of the solubility of humus in alkalies we refer to the formation of the alkali salts of humic acid. To bring out the close similarity between the inorganic portion of the soil and humus we can study the formation of humic acid and humates potentiometrically.

Humates of Alkali Metals

Alkali humates are soluble in water and may be the basis of formation of other humates. The best method of studying the formation of alkali humates is to follow the titration curves of humic acid with alkali hydroxides. Such titration curves are shown in Figure 79.

In view of the fact that the neutralization of a weak acid with a strong alkali takes place when the pH value is raised by 4 pH units, the neutralization of humic acid takes place at pH 7.5. It will be noticed that a faint but distinct point of inflection occurs in the neighborhood of this pH in all the curves in Figure 76. The trend of the curve, however, shows that we are probably dealing with a mixture of humic acids of slightly different dissociation constants. It is also not unlikely that, as in soils, we may be dealing with dibasic acids. However, the exact nature of the mixture of acids or their basicity is not vital to the argument. The main consideration is

that the titration curve is definite, not with one alkali but with all, and the slight differences noticed in the case of individual alkalies are well known in the case of soluble acids.

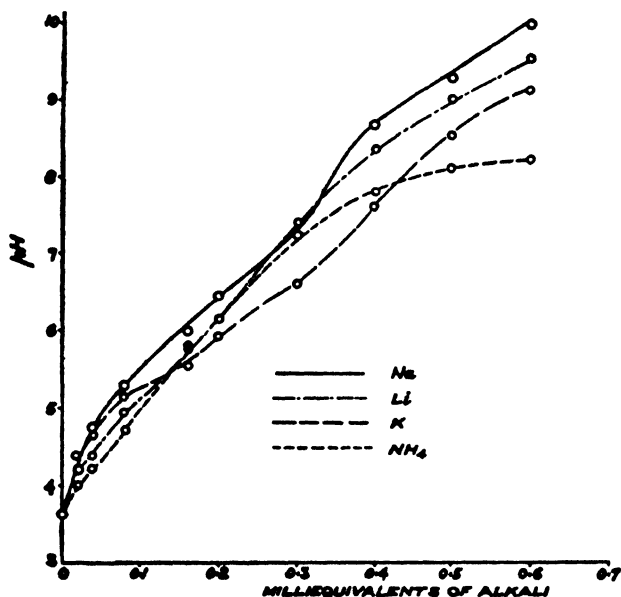



Fig. 79. Titration Curves of Humic Acid with Alkali Hydroxides

Humic acid 0.1 gram

Humic Acid

Humic acid is formed by the action of dilute acid on alkali humates. The course of its formation from Na humate by HCl is shown in Figure 80 (titration curve) and Figure 81 (precipitation curve).

It is seen that the complete precipitation of humic acid takes place when an amount of acid equivalent to the Na in the humate has been added. Thus if we take sodium humate of different pH values, the titration curves are the same, but the precipitation curves shift to the right or left, so that more or less acid is required for the precipitation. The precipitation of humic acid with HCl is completed at approximately pH 1.8. The beginning of the precipitation, however, depends on the pH of the Na humate, occurring at a higher pH value for Na humate of a lower pH value, and vice versa. It is also seen that humic acid is partly soluble even at a pH value as low as 1.5.

Humates of Alkaline-Earth Metals

Ca, Mg and Ba humates can be prepared by the direct neutralization of humic acid with the corresponding hydroxides or by the addition of soluble alkaline earth salts to Na humate. The former reaction can be followed accurately from the titration curves of humic acid with alkaline-earth hydroxides.

$AlCl_3$
$FeCl_3$
HCl

pH

MILLIEQUIVALENTS OF H, FE, OR AL

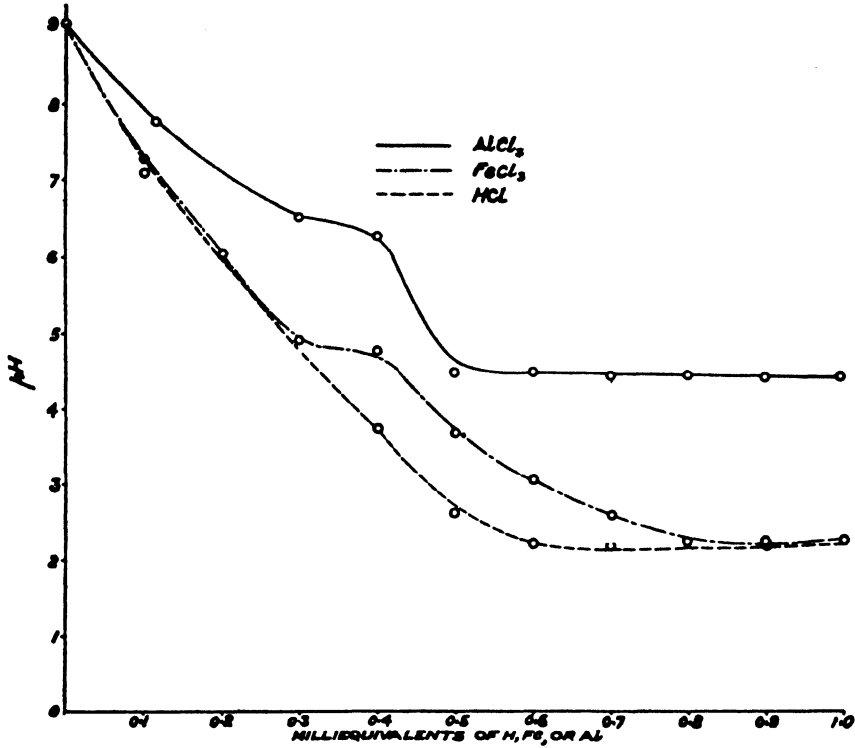



Fig. 80. Titration Curves of Sodium Humate with HCl, $FeCl_3$, and $AlCl_3$
Sodium humate 0.1 gram

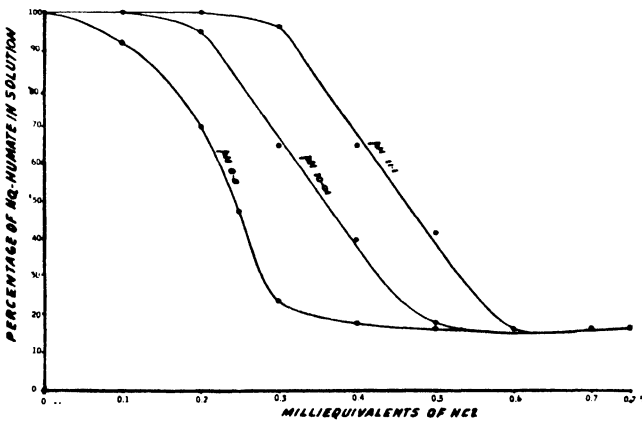



Fig. 81. Formation of Humic Acid from Sodium Humate
Sodium humate 0.1 gram

As in soil, insoluble humic acid can react with alkaline-earth hydroxides and give perfect titration curves, in spite of the fact that the reaction products are also insoluble. (Figure 82).

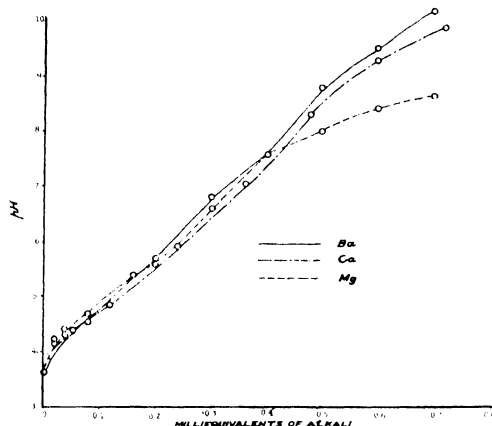



Fig. 82. Titration Curves of Humic Acid with Alkaline Earth Hydroxides
Humic acid 0.1 gram

The precipitation of alkaline-earth humates with the corresponding chlorides was also followed potentiometrically. Increasing amounts of $CaCl_2$, $MgCl_2$ and $BaCl_2$ were added to Na humate solution and shaken for 24 hours, though 2 hours' shaking is sufficient. The pH value of the mixture was determined by the glass electrode, after which the mixture was filtered. An aliquot of the filtrate was taken and humus was determined by the alkaline permanganate method to be described later. The results are plotted in Figures 83 and 84, the former giving the pH changes during precipitation and the latter indicating the amount of humus precipitated as humate and that remaining in solution. It is seen that Ba humate is the least soluble and that Mg humate is appreciably soluble.

A careful examination of Figures 83 and 84 reveals that a break in the titration curve corresponds to the point at which precipitation of the humate begins. The difference is not very great perhaps, but the abrupt change indicates that the humates of the alkaline-earth metals are precipitated in the colloidal state when the pH is high, and they subsequently precipitate when the pH value is reduced below a certain minimum. The gradual lowering of the pH value during the addition of alkaline-earth salts is partly due to the salt effect and partly to the gradual diminution in the concentration of sodium humate. The non-precipitation of humates at higher pH values may also be due to the peptizing action of the sodium humate. This is confirmed by the fact that the solubility of alkaline-earth humates in water is greatly enhanced by the addition of Na humate. This increased solubility, however, depends on the pH value of Na humate: the higher the pH value the greater the

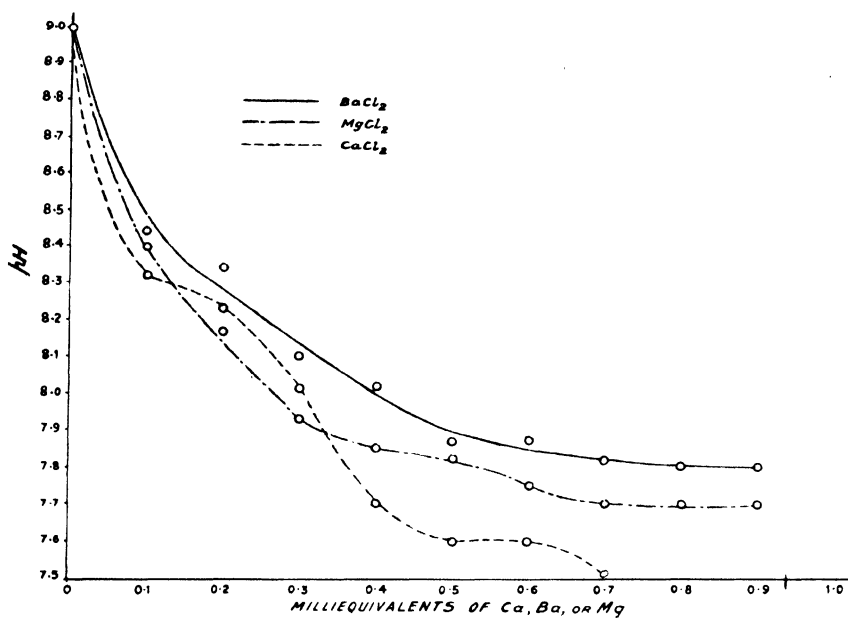



Fig. 83. Titration Curves of Sodium Humate with $CaCl_2$, $BaCl_2$, and $MgCl_2$
Sodium humate 0.1 gram

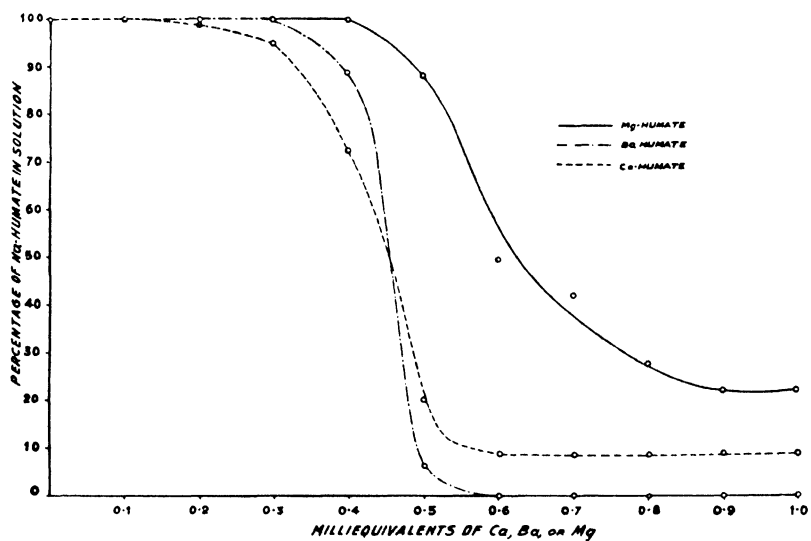



Fig. 84. Formation of Ca, Ba, and Mg Humates from Sodium Humate
Sodium humate 0.1 gram

solubility. This will be clear from Table 81, which gives the solubility of alkaline-earth humates in Na humate of varying pH values.

One-tenth gram of the humate was shaken with 20 cc of water containing 0.1 gram of Na humate. The results are expressed in percentage of the alkaline-earth humate dissolved on shaking, the amount brought into solution being determined by titration with alkaline permanganate. It is seen that the peptization is highest with Mg humate and lowest with Ba humate. This is exactly what would be expected from the precipitation curves given in Figure 84. It must be pointed out that the solubility of alkaline-earth humates in water is greatly reduced by the addition of the corresponding salts. This will be clear from a comparison of Figure 84 and Table 81.

Table 81. Peptization of alkaline-earth humates by Na humate

pH of Na humate	Percentage peptization		
	Ca	Ba	Mg
8.19	36.1	49.0	55.8
9.17	57.6	50.5	66.6
10.62	90.0	62.0	92.5
Water	24.8	11.6	52.5

Iron and Aluminum Humates

Humates of Fe and Al can be prepared by the addition of $FeCl_3$ and $AlCl_3$ to a solution of Na humate. The titration curves of Na humate with $FeCl_3$ and $AlCl_3$ are given in Figure 80 along with that for HCl, to which they are similar. In the Fe and Al curves there is an indication of a point of inflection near the equivalent point. One cannot, however, be sure whether the addition of $FeCl_3$ or $AlCl_3$ results in a chemical compound or merely in the simultaneous precipitation of humic acid and iron or aluminum hydroxide. Such a co-precipitation would result in an intimate mixture of the two compounds. If equivalent concentrations had been employed, the resulting precipitate would contain iron and aluminum hydroxide and humic acid in stoichiometric proportions; but the stoichiometric proportion would be no proof of chemical combination in this case. If alkali or sodium humate is in excess, the stoichiometric proportion of the precipitate will not hold. As weak alkalies, like iron and aluminum hydroxides, can have but a loose combination with a weak acid like humic acid, the existence or absence of stoichiometric relationship would be no proof for or against their chemical combination.

For instance, in the formation of humic acid by the addition of HCl to Na humate (Figure 81), the precipitation, as we have seen, does not commence until a considerable amount of HCl has been added. In other words, we can have Na humates entirely in solution at different pH values. These humates, if neutralized with $AlCl_3$ or

$FeCl_3$, will require different amounts of the latter for complete precipitation of the humate. The precipitated Al or Fe humates,

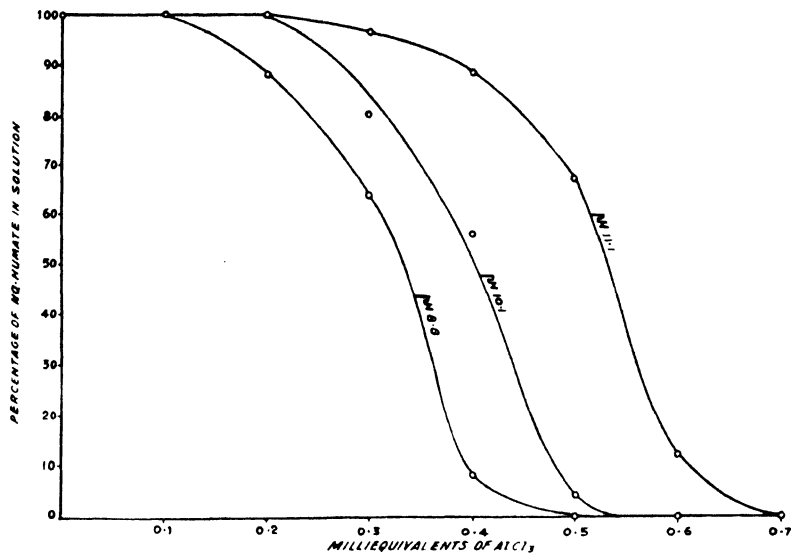



Fig. 85. Formation of Aluminum Humate from Sodium Humate
Sodium humate 0.1 gram

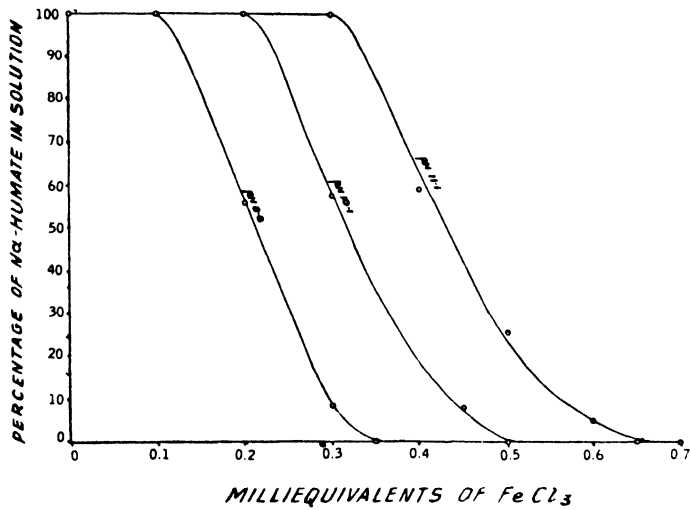



Fig. 86. Formation of Ferric Humate from Sodium Humate
Sodium humate 0.1 gram

however, will contain different proportions of Al or Fe, depending on the pH value of the humate. This is indicated in a striking manner in Figures 85 and 86, which show the precipitation of Al and Fe

humates from Na humate by the gradual addition of $AlCl_3$ and $FeCl_3$, respectively. The precipitation of Al and Fe humate is complete in every case when an amount of $AlCl_3$ or $FeCl_3$ equivalent to the Na in the Na humate has been added. The resulting precipitates of Al and Fe humates, therefore, contain different amounts of Al or Fe.

This is an important point that must be borne in mind by all those seeking stoichiometric proportions in such compounds. The neutralization of acids is a continuous function of the H ion concentration. What is true of soluble acids is also true of insoluble acids or acidoids. Insoluble humic acid can be neutralized with insoluble $CaCO_3$, with the precipitation of insoluble Ca humate. This neutralization follows a titration curve (Figure 87), but the

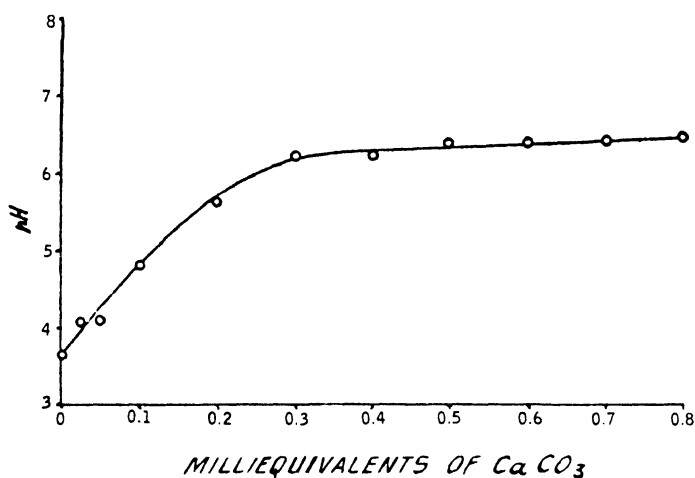



Fig. 87. Titration Curve of Humic Acid with $CaCO_3$
Humic acid 0.1 gram

resulting Ca humate at every step will contain varying amounts of Ca humate, and in fact is a solid buffer solution. These perfectly normal compounds are sometimes wrongly designated as adsorption complexes, because of the lack of stoichiometric proportions.

We have at our disposal an independent line of attack on the question whether Fe and Al humates represent chemical compounds or mere mixtures. We can determine the solubility of these compounds in water and alcohol. As a matter of fact, the solubility in alcohol has been used by other workers for the so-called fractionation of humus. In the first instance from a study of the precipitation of Fe and Al humates from Na humate it is seen that, whereas humic acid is soluble even at pH 1.5, Fe and Al humates are completely precipitated at a pH value of approximately 3.5. This, however, is not conclusive because in the case of Na humate and HCl we have the base NaOH competing between two acids, and even at low pH values we are bound to have a certain proportion of Na humate.

The solubility of humic acid and humates in water and alcohol, however, gives a conclusive answer in favor of the formation of a definite compound, as will be seen from Table 82.

The solubilities were determined by shaking 0.1 gram of humic acid and of humates with 20 cc of water and alcohol (95 per cent) at room temperature (28 – 30°C). No attempt was made to obtain absolute values. The results are expressed in terms of the percentage of humus gone into solution and obtained by filtration and titration of the filtrate by alkaline permanganate; 100 per cent, therefore, does not represent the upper limit of solubility, but 0 per cent does show that the substance is completely insoluble. The fact that humic acid is 100 per cent soluble in alcohol and that Fe and Al humates

Table 82. Solubility of humic acid and of humates in water and in alcohol

Nature of humus	Humus dissolved in 20 cc. from 0.1 gm. (per cent)	
	in water	in alcohol
Humic acid	11.6	100
Na humate	100	3.9
K humate	100	4.2
Li humate	100	22.8
NH_4 humate	100	5.2
Mg humate	45.5	6.7
Ca humate	21.1	0
Ba humate	9.7	0
Fe humate	0	0
Al humate	0	0

are completely insoluble leads one to the only logical conclusion, i.e., that we are dealing with different compounds in the two cases. Any type of mechanical mixture of the hydroxides of Al and Fe and humic acid would certainly have brought some humic acid into solution.

These results are important from two points of view. It is obvious that soils must contain humic acid and humates and that any attempt at their fractionation based on the solubility of these salts in one or the other solvent is bound to be misleading. A good deal of the earlier work based on the soluble and insoluble fractions in one or the other solvent must be revised in the light of these results. Secondly, the close similarity between soil acidoids and humic acids, so well brought out by these results, tends to show that in the case of Fe and Al silicates we are also dealing with chemical compounds, for which independent evidence has already been quoted in the foregoing.

Frequent reference has been made to the estimation of humus by oxidation with alkaline permanganate. A brief account of the method, therefore, seems desirable.

During recent years wet combustion methods for the estimation of humus in soils have become very popular among soil scientists; of these the titration method of Walkley and Black is the simplest and best known. The oxidizing agent in this case is potassium dichromate in acid solution. Apparently there is no reason why oxidation with $KMnO_4$ should not prove equally satisfactory as a means of estimating humus. The earlier methods of estimating humus by $KMnO_4$ oxidation were based on titration of the alkaline extracts. Aschman and Faber extracted the soil with 5 per cent NaOH solution on a water bath and oxidized the extract with 0.01N $KMnO_4$. Fallot modified the procedure and as a preliminary treated the soil with nitric acid to remove the bases, and then extracted it with 10 per cent KOH solution. Similar methods, slightly modified, were proposed by Springer and also by Kreulen. Vincent showed that the nature of the alkali used for extraction of the humus influences the amount of $KMnO_4$ required for titration. More recently, Nostitz investigated Kotzmann's method, which consists in oxidizing 0.2 to 1 gram of soil with 0.025N $KMnO_4$ in 30 per cent H_2SO_4 for 15 minutes at the boiling temperature, adding excess of 0.1N oxalic acid and titrating residually with standard $KMnO_4$. The method was found unsuitable for soils rich in $CaCO_3$.

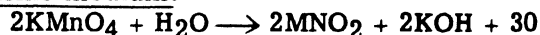
A careful examination reveals the fact that, except for the last, all these methods are based on the preliminary alkaline extraction of the humus. It is well known that alkalies do not extract all the humus. Besides, these experimenters used excessive concentration of alkalies; Nostitz, on the other hand, used an excessive amount of acid. It does not seem to have been generally recognized that excessive alkalinity or acidity can decompose $KMnO_4$, leading to erroneous results. This is illustrated in a striking manner in Figure 88, in which are plotted results of an estimation of Merck's humic acid.

A standard solution was estimated by $KMnO_4$ oxidation in the presence of varying proportions of NaOH or H_2SO_4. It will be seen that there is a definite range beyond which the results are erroneous with both alkaline and acid solutions. The failure of the $KMnO_4$ oxidation has been mainly because this fact has been overlooked. Another important point that must be borne in mind is the concentration of $KMnO_4$. A dilute solution of $KMnO_4$, such as 0.1N solution, undergoes rapid decomposition in a highly alkaline medium, but a normal solution can withstand higher alkalinity without decomposing. It should be remembered that this process of oxidation is different from that in an acid solution, as is shown in the following equations.

Acid medium:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

Alkaline medium:

$$2KMnO_4 + H_2O \longrightarrow 2MNO_2 + 2KOH + 3O$$

Thus larger amounts of permanganate are required for oxidation in an alkaline medium than in an acid medium. A description of the procedure finally adopted follows.

One to two grams of the soil, depending on the amount of humus, is boiled with 20 cc N $KMnO_4$ in 0.05N NaOH. More of the alkaline $KMnO_4$ solution is added if the color of the solution is destroyed within ten minutes of boiling. After the oxidation is complete, the $KMnO_4$-treated material is made up to volume and filtered. To 50 cc of the filtrate, sulphuric acid and excess of oxalic acid are added and titrated residually with $KMnO_4$. Each cubic centimeter of normal alkâline permanganate equals 3.9 mgm of carbon.

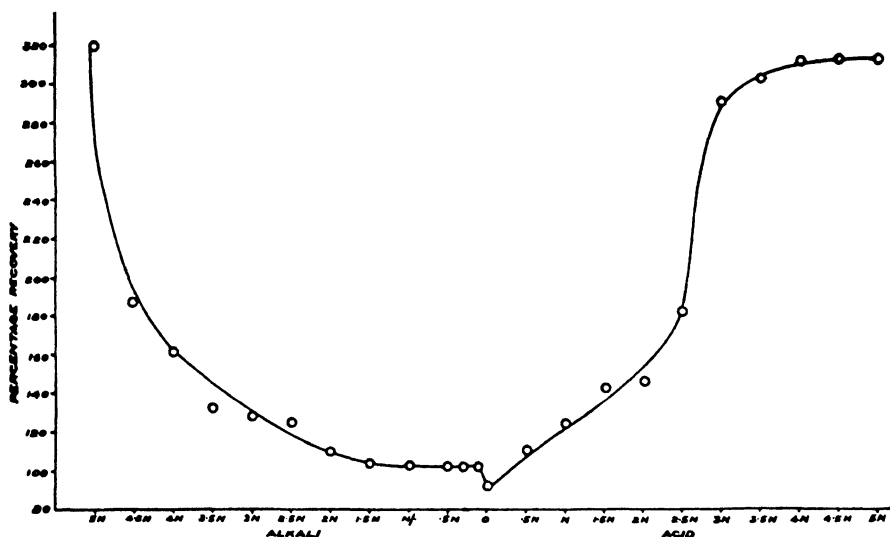



Fig. 88. Recovery of Humus by $KMnO_4$ Oxidation in Acid and Alkali Solutions

The permanganate method as outlined is perhaps no improvement on Walkley and Black's method in regard to simplicity and rapidity, but the important point is that by two different methods of oxidation practically identical results are obtained. Whatever the nature of humus and its various fractions it is unlikely that we are measuring by oxidation something vastly different from the actual material.

Extraction of Humus from Soils with Alkalies

Extraction of humus from soils with alkalies was well known even in the very early days of soil science, and as pointed out before almost all the methods of estimating humus were based on its solubility in alkalies, which were subsequently replaced by rapid oxidation methods.

Apart from its estimation, the solubility of humic acid and various humates must be studied with reference to the pH value of the

medium, a factor entirely ignored by almost all the workers in this field. Merck's "pure humic acid" was used for this purpose: 0.1-gram portions of humic acid were shaken for 24 hours with increasing amounts of alkalies and pH values determined with the glass electrode. It was then filtered and humus determined in the filtrate by the alkaline permanganate method (Figure 89). It will be seen that the solubility depends on the nature of the alkali and the pH value of the medium. All alkali hydroxides are almost equally effective. Of the alkaline-earth hydroxides $Mg(OH)_2$ is the only one that can extract humus, though the solubility of Mg humate is less than that of alkali humates.

It must be admitted that alkaline-earth hydroxides have never been used for humus extraction, but the results have been included in this study to emphasize the fact that alkaline extraction of humus is essentially a process of humate formation and that the efficacy of a particular alkali depends on the solubility of the humate formed. The part played by pH value, though important, is secondary in the sense that it marks the various steps in the conversion of the insoluble humic acid into soluble humates, which process seems to be completed at just about the neutral point, i.e., pH 7. It is interesting to note that apparently there is no justification for using alkalies of high concentration for humus extraction, since maximum solubility is obtained at pH 7. This is approximately equal to 20 cc of 0.02N alkali for 0.1 gram of humic acid; therefore, if a soil contains 10 per cent of humic acid, it should not require more than 100 cc of 0.04N alkali solution per 10 grams for the complete extraction of humic acid, provided the soil has no disturbing influence.

Solubility of Humates in Alkalies. NaOH, NH_4OH and Na_2CO_3 are the most important alkalies used for the extraction of humus from soils. Since all the humus in soils cannot exist as humic acid, it is necessary to know how the various humates respond to alkali extraction. Tenth-gram portions of various humates were shaken for 24 hours with increasing amounts of different alkalies and the humus dissolved was determined after filtration by oxidation with alkaline permanganate as usual (Figure 89). It will be seen that different humates respond differently to alkali treatment. The superiority of Na_2CO_3 to NaOH for extracting alkaline-earth humates is obvious from the fact that the former results in the formation of the insoluble alkaline-earth carbonate. The superiority of NH_4OH to all other alkalies in extracting Fe humate is very interesting, and indicates the specific influence of each alkali on different humates. The uniformity of alkaline extraction of humic acid, unlike the humates, suggests the advisability of preliminary treatment of the soil with acid to convert all the humates into humic acid. To see if this conversion is possible, various humates were leached with 0.05N HCl. It was found that in all cases the basic radical was completely removed, leaving the humic acid behind.

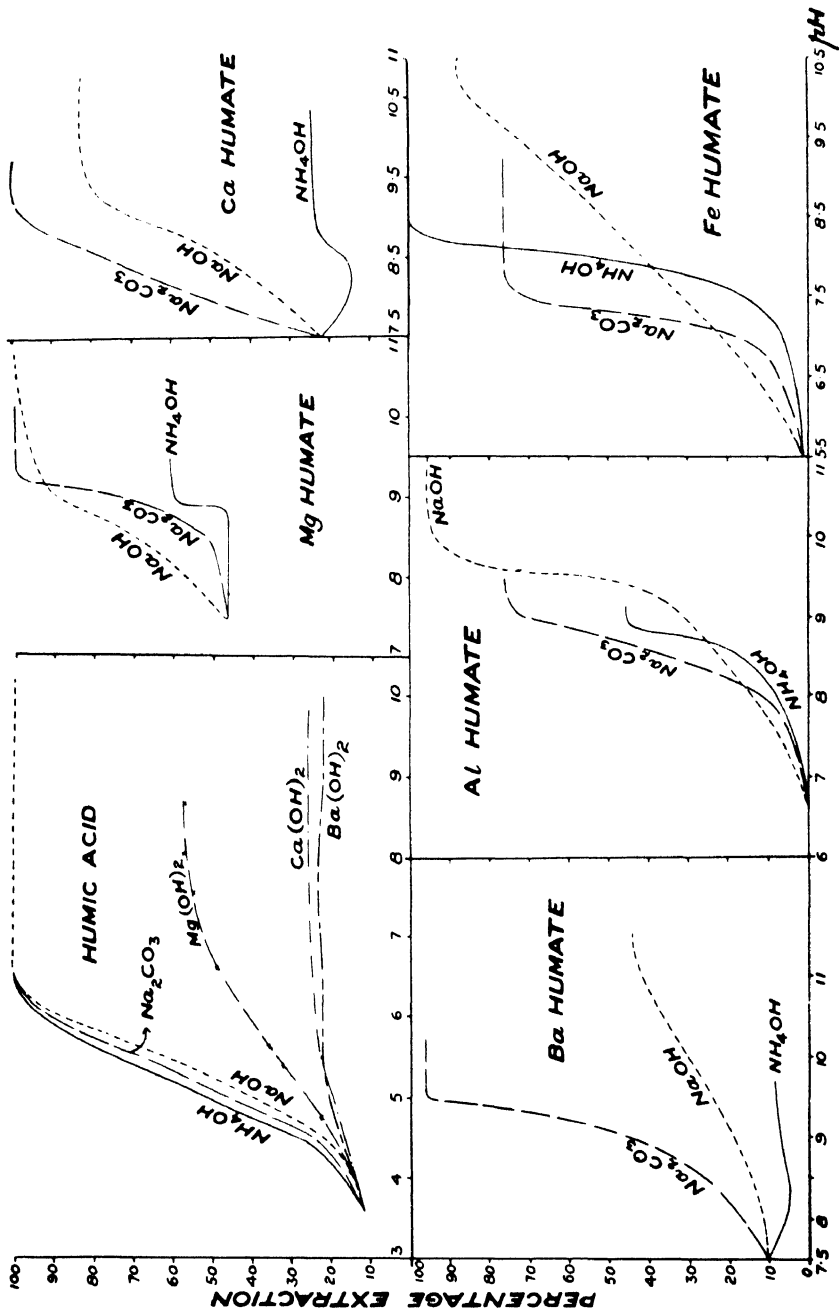



Fig. 89. Solubility of Humic Acid and Humates in Different Alkalies

Extraction of Humus from Soils by Alkalies

A black cotton soil of high base-exchange capacity and containing 4.63 per cent humus was selected for this study in the first instance. It was treated with 0.05N HCl to convert all the natural humates to humic acid, followed by leaching with water. Five-gram portions of the treated soil were shaken for 24 hours with different alkalies of varying concentration. The relation between pH value and humus extracted (expressed as percentage of total humus in the soil, as determined by the alkaline permanganate oxidation) is shown in Figure 90, which indicates that with all alkalies practically no humus is extracted up to pH 5. It may be that up to this pH the soil takes up all the alkali and no humate is formed, or that the formation of the humate is itself restricted irrespective of the soil.

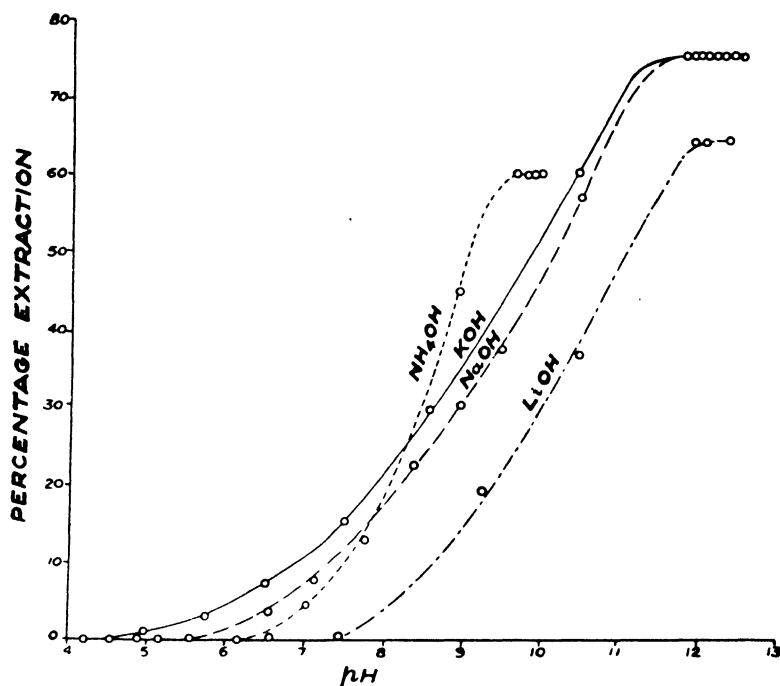



Fig. 90. Relation between pH Value and Humus Extracted by Different Alkalies

It also appears that all the organic matter cannot be extracted from a natural soil by treatment with alkalies in the cold. The effect of time, temperature and strength of alkali on the extraction of humus from the soil was, therefore, studied systematically. Since the extraction referred to one soil under varying experimental conditions, humus was estimated colorimetrically. The effect of temperature and the strength of alkali on the extraction of humus is summarized in Table 83. It will be seen that the strength of alkali can be varied from 0.1N to 2N without any effect. Apparently there is no justification for using alkali stronger than 0.1N or 0.2N with

respect to NaOH and Na_2CO_3. It is also clear that NaOH or Na_2CO_3 cannot extract as much as a mixture of both. It is important that the exact part played by Na_2CO_3 should be well understood. Its main function lies in converting Ca and Mg humates into Na humates

Table 83. Effect of temperature and strength of NaOH-Na_2CO_3 mixture on the extraction of humus

Strength of NaOH solution	Strength of Na_2CO_3 solution						
	0.1N		0.2N		0.5N		0
	70°C	20°C	70°C	20°C	70°C	20°C	70°C
	Percentage of total humus extracted						
2N	82.0	26.1	82.0	26.5	80.1	25.6	50.5
N	81.8	21.7	82.0	22.3	75.5	22.2	20.3
0.2N	81.8	21.9	81.8	22.0	39.1	21.8	16.3
0.1N	81.8	22.0	81.8	21.0	39.0	21.5	4.9
0.05N	81.5	21.6	81.0	20.1	27.3	19.1	0
0	59.3	20.9	37.3	18.7	20.5	17.3	0

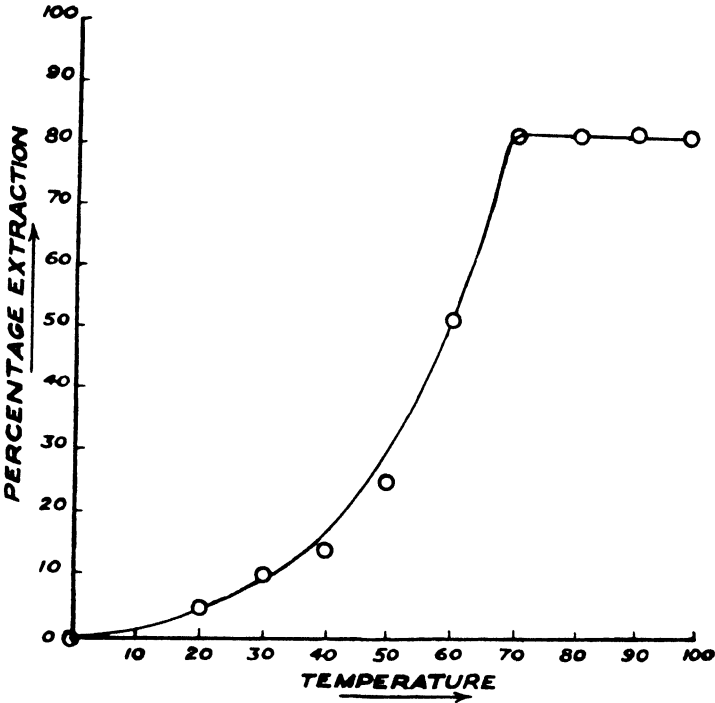



Fig. 91. The Effect of Temperature on the Extraction of Humus

and the precipitation of $CaCO_3$. The temperature has a profound influence on extraction which should be kept above 70°C to obtain maximum extraction. This will be clear from Figure 91. A NaOH-Na_2CO_3 mixture 0.2N with respect to each was used. It is seen that

at $0^{o}C$ humus is completely insoluble in alkali. This observation is very important. In the estimation of Ca saloid in humus soils the extraction with K acetate-oxalate-carbonate mixture yields a colored liquid which interferes with subsequent titration of the extract with $KMnO_4$. If, however, the extraction is carried out at $0^{o}C$, the filtrate is only slightly colored and does not interfere with the $KMnO_4$ titrations. A striking feature of all these results is the concordance of the values for maximum extraction, which shows that a definite percentage of the total organic matter is capable of being extracted by alkali.

The effect of time of shaking on the amount of humus extracted was studied. It was found that maximum extraction in the cold is obtained in 8 hours and above $70^{o}C$, in 30 minutes. The remarkable thing is that the amount of humus extracted in the cold reaches a maximum which does not increase on longer shaking, but as soon as the temperature is raised, this maximum reaches another constant but of very much higher value.

It is interesting to note that whatever the treatment it is not possible to extract all of the organic matter from this soil. However, from an examination of a number of soils it appears that this is by no means universally true. In some soils all of the humus is extracted and in others only 60 to 80 per cent. It is apparent that in wet oxidation organic matter which is not completely humified is attacked, whereas in alkaline extraction only the humified organic matter is dissolved out or forms humates.

Waksman, who studied the extraction of humus with alkali, divided humus into two fractions. The portion of the organic matter that was soluble in alkalies and precipitated by acids he called "alpha" fraction. When the acid solution obtained after this fraction has been removed is neutralized with an alkali, another precipitate is formed, which is soluble both in alkali and in acid; Waksman termed this the "beta" fraction of soil organic matter. It may be remembered that the "alpha" fraction, which is light brown in color and not black as is the "beta" fraction, contains only 30% of organic and 70% of inorganic matter, largely aluminum. It does not seem right that a substance containing 70% of inorganic matter should be designated "organic matter" – much less a fraction of humus. The fallacy underlying this conception must be ascribed to the lack of appreciation of the role of inorganic materials in humus. When it is remembered that humus in soils exists as humates of which Fe and Al humates form quite a substantial portion, the genesis of the "beta" fraction becomes clear. As a matter of fact, the so-called "beta" fraction is nothing but Fe and Al humates mixed with varying proportions of free alumina. Such a mixture is soluble in both acids and alkalies and has an isoelectric zone very near to that ascribed to the "beta" fraction. The phenomenon could be easily demonstrated by taking various humates and mixtures of humic acid and Fe and Al humates in varying proportions and subjecting

these to Waksman's extraction process. Varying proportions of the fraction will result in the case of Fe and Al humates, but no such fraction appears in humic acid or other humates.

Colorimetric methods of estimating humus in soils have been developed and used by several workers. An excellent review of these is given in Waksman's treatise on humus. The obvious defects of these methods lie in the fact that all of the humus cannot be brought into solution by alkaline extraction, on which these methods depend. As a matter of fact, the technique of alkaline extraction has been so varied and defective that any method based on it must suffer from this initial disadvantage. However, with the improved method of extraction with 0.2N NaOH and Na_2CO_3 it is possible to determine colorimetrically the humus in the soil which is soluble in alkalies. The standard color may be taken as an extract from any one soil in which humus is determined by the alkaline permanganate method. From a comparison of more than a hundred soils it was concluded that the colorimetric method compared well with the permanganate oxidation method. The agreement is not so close as would be desired in exact analytical procedure; however, the quick oxidation methods of estimating humus are themselves not very exact and greater accuracy for a substance like humus, so unevenly distributed in soil, is hardly to be expected.

It may be mentioned that when the humus content of a soil is above 6% all of it cannot be extracted with alkali in the ratio of 5:100. For such soils leaching with the alkalies must be resorted to, or the proportion of alkali must be increased to 1:100 for complete extraction.

It is a remarkable fact that natural forces have created humus in soils, which is very similar to the ferroaluminosilicates in its various physicochemical reactions – so much so that almost every reaction possible with silica and silicates can be reproduced in the case of humic acid and humates. The differences, if any, are merely qualitative, so that for most purposes we can treat humus as an integral part of the soil. Quantitatively, of course, humus is much more reactive, but this can only result in imparting to the soil somewhat greater reactivity without causing any fundamental change in its chemical properties as a whole.

PART II

MECHANICAL ANALYSIS OF SOILS

CHAPTER I

INTRODUCTORY

When we look at a soil the first thing that strikes us is its texture. It is difficult to define texture: roughly speaking, it may be described as the degree of coarseness. More precisely, it is related to the relative proportion of particles of various sizes. The process by which this is determined is known as mechanical analysis.

The history of the principles and methods of mechanical analysis extends back to ancient Greece, when apparently decantation methods for separating particles were known; but no applications of these were made to soils or sediments until 1692. Sieves were used to separate sands in 1704. The need of understanding the composition of earths for classification was recognized in 1750, and the earliest recovery of three grades by sedimentation occurred in 1784. The term "mechanical analysis" was introduced in 1805. The first rising current elutriator was used in 1839. In 1851 Stokes' law was formulated; in 1867 it was applied to mechanical analysis. The earliest use of graphs to represent sediments was in 1892. In the same year the centrifuge was applied to mechanical analysis. Air analyzers were introduced in 1906. In 1912 simple sedimentation balance appeared, and a mathematical theory of sedimenting systems was developed. The first manometric tube was introduced in 1918. The pipette method was developed in 1922 and the hydrometer in 1927.

Until recently no attention was paid to the methods of dispersing soil preliminary to mechanical analysis. Even now opinion is divided as to the value of dispersing methods which aim at revealing the ultimate structure of the soil. Such drastic methods as acid treatment, it is argued, ill conform with the behavior of the soil in the field and by presenting a false picture obscure the main object of mechanical analysis. Others contend that the state of aggregation of a soil is but one phase in its dynamic history. There is no doubt that either the soil should be subjected to the least disturbance and the size distribution of particles as they exist in the field determined, or the treatment should be sufficiently "drastic" to break down all the compound particles into ultimate units and yet not so drastic as to cause mechanical breakdown of these ultimate units into still smaller particles. Opinion, however, will again be divided as to

the definition of "ultimate" units. We have so far been taking the maximum clay as representing the "ultimate units", but as we shall explain later, the conventional clay is only the upper limit of a series of finer fractions which profoundly affect the physicochemical properties of the soil in general and the so-called clay fraction in particular.

Methods of mechanical analysis may be grouped under the following general heads:

(1) Decantation or beaker methods
(2) Rising current elutriators
(3) Air analyzers
(4) Sedimentation methods using automatic weighing machines
(5) Sedimentation methods using manometric tubes
(6) Pipette methods
(7) Hydrometer methods
(8) Centrifugal sedimentation methods and ultramechanical analysis
(9) Siltometer for the mechanical analysis of sands and silts

The majority of the above methods, of which a very brief description will suffice, are of historical interest only; those in everyday use will be described in greater detail.

The fundamental basis of all methods of mechanical analysis of soils is Stokes' law giving the relation between the size of particles and their settling velocity in water or in any other liquid for that matter:

$$v = 2/9g \frac{\delta - \delta'}{\eta} r^2$$

wherein

v = rate of fall in centimeters per second
g = gravitational constant
δ = density of particles (2.68)
δ' = density of water (1.00)
η = viscosity of water
r = radius of the particles

It will be seen that for a certain value of r the velocity of fall v varies inversely as the viscosity of water η, and as η varies considerably with the temperature, the results of mechanical analysis will be untrustworthy unless proper attention is paid to this variable. These variations can be accounted for by means of the data given in Table 1 where the settling velocity of all particles between 0.001 and 0.1 mm diameter has been calculated for temperatures between 10 and 35^{o}C. These are the extremes of temperature met with, even in the tropics.

As we may find particles of all shapes in soils it seems desirable

Table 1. Rate of settling of particles at various temperatures

Diameter mm.

.001	.002	.003	.004	.005	.006	.007	.008	.009	.01	.02	.03	.04	.05	.06	.07	.08	.09	.1
Hours				Minutes						Seconds								
40.80	10.19	4.53	2.55	98.0	68.0	53.0	38.3	30.2	24.5	367	163	92	59	40.8	31.8	22.9	18.1	14.7
39.64	9.91	4.40	2.48	95.2	66.1	51.5	37.2	29.3	23.8	357	158	89	57	39.6	30.9	22.3	17.6	14.3
38.55	9.63	4.28	2.41	92.6	64.2	50.1	36.1	28.5	23.1	347	154	87	55	38.5	30.0	21.7	17.1	13.9
37.48	9.37	4.16	2.34	90.0	62.5	48.7	35.1	27.7	22.5	337	150	84	54	37.5	29.2	21.1	16.7	13.5
36.39	9.10	4.04	2.28	87.6	60.8	47.3	34.2	27.0	21.9	328	146	82	52	36.4	28.4	20.5	16.2	13.1
35.45	8.86	3.93	2.22	85.1	59.2	46.1	33.3	26.2	21.3	319	142	80	51	35.4	27.6	19.9	15.8	12.7
34.49	8.62	3.83	2.16	82.8	57.6	44.9	32.4	25.5	20.7	310	138	78	50	34.5	26.9	19.4	15.3	12.4
33.64	8.41	3.73	2.10	80.8	56.1	43.7	31.5	24.9	20.2	302	134	76	48	33.6	26.2	18.9	14.8	12.1
32.73	8.18	3.64	2.04	78.6	54.6	42.5	30.7	24.2	19.6	294	131	74	47	32.7	25.5	18.4	14.5	11.8
31.89	7.98	3.54	1.99	76.6	53.2	41.4	29.9	23.6	19.1	287	127	72	46	31.9	24.8	17.9	14.1	11.5
31.10	7.77	3.45	1.94	74.6	51.8	40.4	29.1	23.0	18.6	280	124	70	45	31.1	24.2	17.5	13.8	11.5
30.28	7.57	3.36	1.89	72.7	50.6	39.4	28.4	22.4	18.2	273	121	68	44	30.3	23.6	17.0	13.4	10.9
29.55	7.38	3.28	1.85	70.9	49.3	38.4	27.7	21.8	17.7	266	118	66	42	29.5	23.0	16.6	13.1	10.6
28.81	7.21	3.20	1.80	69.2	48.1	37.5	27.0	21.3	17.3	259	115	65	41	28.8	22.4	16.2	12.8	10.4
28.12	7.03	3.12	1.76	67.5	46.9	36.6	26.4	20.8	16.9	253	113	63	40	28.1	21.9	15.8	12.5	10.1
28.78	6.86	3.05	1.72	65.9	45.8	35.7	25.8	20.3	16.5	247	110	62	39	27.8	21.4	15.5	12.2	9.9
26.81	6.71	2.98	1.68	64.4	44.7	34.8	25.2	19.8	16.1	241	107	60	39	26.8	20.9	15.1	11.9	9.6
26.19	6.54	2.91	1.64	62.9	43.7	34.0	24.6	19.4	15.7	236	105	59	38	26.2	20.4	14.7	11.6	9.4
25.60	6.40	2.84	1.60	61.4	42.7	33.2	24.0	19.0	15.4	231	102	58	37	25.6	19.9	14.4	11.4	9.2
25.04	6.25	2.78	1.56	60.1	41.7	32.5	23.4	18.5	15.0	226	100	56	36	25.0	19.4	14.1	11.1	9.0
24.46	6.12	2.72	1.53	58.8	40.8	31.8	22.9	18.1	14.9	221	98	55	35	24.5	19.0	13.8	10.8	8.8
23.95	5.98	2.66	1.50	57.5	39.9	31.1	22.4	17.7	14.4	216	96	54	34	23.9	18.6	13.5	10.6	8.6
23.44	5.86	2.60	1.47	56.3	39.1	30.4	21.9	17.3	14.1	211	94	53	34	23.4	18.2	13.2	10.4	8.5
22.95	5.74	2.55	1.44	55.1	38.3	29.8	21.5	17.0	13.8	206	92	52	33	22.9	17.8	12.9	10.2	8.4
22.50	5.62	2.50	1.41	54.0	37.5	29.2	21.1	16.6	13.5	202	90	51	32	22.5	17.5	12.6	10.0	8.1
22.01	5.50	2.45	1.38	52.9	36.7	28.6	20.7	16.3	13.2	198	89	50	32	22.0	17.2	12.4	9.8	7.9

to introduce the conception of "equivalent diameter", which may be defined as the diameter of a sphere of uniform density falling as a sediment in a liquid with the same velocity as soil particles settle under similar conditions. For the presentation of data for routine analyses some workers prefer to use settling velocity as the basis of grouping soil particles. One advantage of this method is that it is direct and the mathematical interpretations become simpler. On the other hand, it is easier to form a mental picture of mechanical analysis in terms of particle size rather than of settling velocity. The use of settling velocity is also open to the objection that the temperature has to be specified; and even if the product of viscosity and velocity is used, this quantity has such peculiar dimensions that one loses that familiarity with the results of mechanical analysis, which one is accustomed to when thinking in terms of size. Throughout this book the diameters of particles are the "equivalent" diameters, as defined by Stokes' equation. It is believed that, unless we are dealing with needles or thin plates, the equivalent diameters will afford a good idea of the real dimensions of particles.

CHAPTER II

DECANTATION METHODS

Decantation methods, as the name implies, consist in stirring a known weight of soil with water and, after allowing it to settle for a definite time, pouring off the supernatant liquid which is supposed to contain particles up to a certain limiting diameter. Repeated stirring and decanting with fresh lots of water results in separating all the particles up to a certain diameter. The combined pourings are either made up to a known volume and an aliquot evaporated to dryness, or the suspension in every case is flocculated by the addition of a small amount of acid, and the precipitated fraction separated by decantation or filtration and weighed after drying at 100 to 100°C, or ignited and weighed. The latter procedure was more prevalent when decantation methods were the order of the day. The soil suspension is made slightly alkaline by the addition of ammonia or sodium carbonate, which helps in the dispersion of the clay particles, so that fewer pourings are necessary.

Ordinary 700-800 cc beakers with spout are quite suitable for the purpose, and it is for this reason that these methods are sometimes spoken of as the beaker methods. The beakers are marked at a height of 10 cm from the bottom, and are filled each time to the mark. Stirring is done with a glass rod having a rubber policeman. With practice and skill, clean pouring of the supernatant liquid can be done; but the method suffers from the defect that there is danger of cumulative errors during repeated pourings. A number of soils can be studied at a time, but separation of the clay fraction alone generally takes 3 or 4 days.

The use of the centrifuge to hasten sedimentation has been advocated by American workers. However, as the centrifugal force varies as the square of the distance from the axis of rotation and as the particles settle in long tubes, they are subject to an increasing force as they move toward the bottom of the sedimentation tube. Not only this, but particles in a uniform suspension start with a different initial velocity. It is therefore doubtful if the use of the centrifuge is really an improvement on the original method which, though slower, is theoretically sound, and can be speeded up by increasing the number of beakers.

The possibility of contaminating the supernatant liquid with the sediment at the time of pouring led to several improvements in sedimentation vessels. Of these the most important is the Atterberg cylinder. With the help of a glass tube attached to the side of a cylinder, the suspension could be drained off at a regulated rate controlled by a pinch-cock. The arrangement prevents contamination of the suspension with sediment, but the separation of the dif-

ferent fractions is not so complete as in the beaker method.

Rising-Current Elutriators

The rising-current elutriators are based on the principle that a particle settling in water with a certain velocity can be made stationary if the water is rising with the same velocity as the particle is falling. Again, if the water is rising with a velocity greater than the settling velocity of the particle, the latter will begin to rise at a rate equal to the difference between its velocity of fall and the velocity of rise of water. Thus if a number of particles of different sizes, and consequently having different rates of settling, are subjected to a rising current of water, the smallest will begin to move upward at a certain critical velocity which is slightly greater than their settling velocity. If the rising current is maintained at a steady rate, all particles smaller than a certain size will be separated from the rest of the particles in course of time. If the velocity of the rising current is increased, another crop of particles corresponding to a larger size will be separated. Thus by gradually raising the velocity of the rising current the various fractions can be separated and weighed.

The simplest form of elutriator was devised by Schöne as early as 1867. The simple one-piece elutriator was later replaced by several types of multiple-tube elutriators. These made use of the principle that the same current of water assumes different rising velocities when passing through conical cylinders of different sizes. The separation of particles of different diameters, therefore, could be effected in one operation.

The elutriator methods are not capable of much refinement. The amount of liquid required for separating the various fractions is so large that the use of distilled water is prohibitive. Separation by ordinary tap water cannot be reliable on account of the flocculating action of the salts present in it. Commercially certain types of elutriators have still some uses in separating different grades of sand, for instance, or for washing sand mixed with clay; but for the mechanical analysis of soils they are altogether obsolete.

Air Analyzers

The use of air currents was only a logical development of the water elutriators, to which they are closely related in principle. The substitution of a fluid several times lighter than water necessarily involved a strain on design, and the technique never reached perfection. Air elutriators have received considerable attention in their application to the study of pigments, cement, and ceramic materials, and in the grading of seeds, but the nature of these materials definitely precludes the use of water. For studying the crumb structure of soils and how it is affected by water, air analyzers might find interesting application, but on the whole they require only passing reference.

CHAPTER III

SEDIMENTATION METHODS

Automatic Weighing Devices

The essential difference between the sedimentation and decantation methods lies in the fact that in the former attention is focussed on that portion of the suspended material which has settled in a given time, whereas in the latter the material remaining in suspension in a given time is considered. One of the most important developments in the history of mechanical analysis of soils is the use of the continuous sedimentation balance devised by Odên and later improved by Keen and his co-workers and known as the Odên-Keen balance. With the help of this balance Oden developed his mathematical theory of sedimenting systems. This theory was further elaborated by him in collaboration with Fisher.

The Odên-Keen balance is an extremely ingenious piece of apparatus. The particles settle on the pan hanging freely in the suspension and the weight of the sediment is automatically recorded in the form of a curve on a graph paper revolving on a drum. The design of such an extremely sensitive instrument held out great promise which was unfortunately not fulfilled. For instance, Coutts and Crowther have discussed a source of error in the method caused by certain currents set up during sedimentation. This source of error could not be eliminated and the automatic balance as an instrument of precision for the mechanical analysis of soils has lost all its importance, though it has still certain uses in industry and research. Similar remarks apply to the automatic balance of Johnson in which the record of the progress of sedimentation is obtained by punching holes in a graph paper on a revolving drum, by sending electric sparks through it at regular intervals.

Manometric Tubes

Closely allied to the weight-recording device are the manometric sedimentation cylinders in which the changes in the hydrostatic pressure of the suspension due to settling are recorded by a sensitive manometer. Wiegner, who introduced this principle, made use of a long cylinder to which was joined through a stop-cock a parallel manometric tube of about the same length. With the stop-cock closed, water was poured into the manometer and the soil suspension in the cylinder. On opening the stop-cock, the manometer registered the hydrostatic pressure of the suspension column and as

the particles settled below the level of the point of junction of the manometer, the pressure dropped. By observing the decrease in pressure as a function of the time, a curve was constructed from which the distribution curve could be computed.

Wiegner's apparatus was improved by Gessner, who added a photographic device for obtaining a continuous record of the curve.

Other modifications were introduced by several workers, chiefly for magnifying the pressure differences. Kelly bent the manometric tube at an angle. Summer used the device with the manometric arm bent horizontally and with benzene as the index liquid. Barnes used a needle geared to a dial on the manometer to obtain precise readings of the water level. Odên used pentane as the manometer fluid

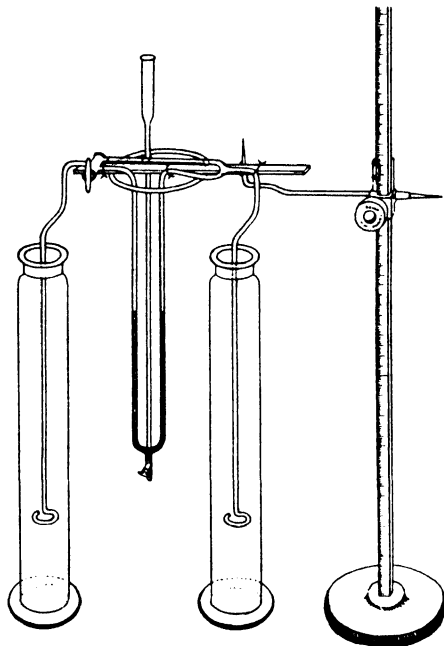



Fig. 1. Diagram of the Manometric Apparatus for the Mechanical Analysis of Soils

and suspended the manometer tube in the main cylinder, thus obviating temperature difference between the two. Crowther introduced a manometric device in which the hydrostatic pressure was measured at two points in the suspension. The distance between them was small, compared to the total length of the settling column. Aniline was used as the index liquid; it measured the density of the suspension at the point midway between the two. The results obtained with this method could be directly converted into a summation curve.

The author has devised a manometric apparatus for the mechanical analysis of soils which has certain novel features. The apparatus shown diagrammatically in Figure 1, is based on the principle

of the differential liquid manometer having a mixture of aniline and benzene (of density slightly higher than that of water) as the heavier liquid and water itself as the lighter liquid. Two cylinders of equal diameter and fitted with ground glass stoppers are used – one to hold the soil suspension and the other water, filled to the same height as the suspension. By means of a three-way tap the connection between the suspension and water column can be established directly or through the manometer as desired. The lower end of the tube that dips into the suspension is spiral-shaped, so that if the suspension enters, it cannot rise above the level of the tip.

The suspension is well shaken and the cylinder placed alongside the one containing water. The apparatus is then lowered to the desired depth and direct connection made between the two cylinders. Since the suspension can support a higher column of water, the level in the water cylinder rises by a few millimeters depending upon the concentration of the suspension and the depth to which the end of the tube has been lowered. After about 3 minutes the tap is turned off and the apparatus taken out. If too much suspension has entered the spiral tube, it is washed out by dipping the other end into a cylinder of water and siphoning it out. The aniline-benzene meniscus is also brought to the lowest point on the manometer tube adjoining the suspension cylinder. The suspension is again shaken and set aside just when a stop watch is started. Since a preliminary leveling of the liquids in the cylinders has already been effected, the connection is established through the manometer. At first there is a slight depression of the meniscus in the tube by the side of the suspension, which soon begins to rise, and steadily moves up as the particles settle down. Its level is noted at suitable intervals, as explained subsequently, either directly or by a scale attached to the manometer tube or by means of a Kathetometer.

If D is the internal diameter of the cylinders and d that of the manometer tube, the magnification is D^2/d^2. For a 1 per cent suspension which has a density of 1.0063, the level of the water will be $1.0063v$ cm higher than that of the suspension when the side tube dips v cm below the surface of the suspension. To produce this difference, however, when both the cylinders are connected the fall in the suspension level and the corresponding rise in the water level must be equal to $0.0063v/2$ cm; and vice versa, the same rise and fall must take place in the opposite direction when the whole suspension settles down. However, this change in the levels of the cylinders will correspond to a movement of the meniscus in the manometer of $D^2/d^2 \times 0.0063v/2$ cm, or when 1 per cent of the total solids in the suspension settles, the manometer will register a change of $D^2/d^2 \times 0.0063v/2 \times 1/100 = a$ cm. In other words, the percentage of any fraction which settles between times t and t' from the beginning of sedimentation will be obtained by dividing the change in the meniscus reading during the above time interval by a. As long as the sedimentation cylinders used are of the same diam-

eter a remains constant. If a 2% suspension is used, then obviously the change in the manometer readings must be divided by $2a$, and so on. Similarly, if the depth of the sedimentation column is altered from v to v' the readings are to be divided by av'/v.

It will be seen that the magnification of the instrument depends on the size of the cylinders, the concentration of the suspension, and the depth of the sedimenting column. By a judicious combination of these the desired magnification to suit any particular requirement can be obtained. In the author's instrument the manometer registered a total change of 33.3 cm for a 2% suspension when the side tube was kept at 30 cm depth, or a change of 3.3 mm corresponded to the settling of 1 per cent of the particles. The manometer tube had an internal diameter of about 6 mm and the cylinders were about 10 cm in diameter and about 45 cm in height.

The method of calculating the results is the same for all such instruments in which the change in density is measured by a manometer. The following exposition may be found simpler by those who have no knowledge of integral calculus.

Suppose a uniform suspension of soil consists of particles of equivalent diameter d_1, d_2, d_3, d_4, d_5....and suppose the concentration of the various groups of particles is A, B, C, D, E....respectively, and the time taken by each individual group to settle 10 cm is t_1, t_2, t_3, t_4, t_5.... If the side tube is dipped in the suspension to a depth of 10 cm and readings of the meniscus are taken after time intervals of t_1, t_2, t_3, t_4, t_5....from the beginning of sedimentation, then the change in the meniscus during the various time intervals will have been brought about by the settling of the particles as follows:

(a) $A + B \times t_1/t_2 + C \times t_1/t_3 + D \times t_1/t_4 + E \times t_1/t_5$ after time t_1

(b) $A + B + C \times t_2/t_3 + D \times t_2/t_4 + E \times t_2/t_5$ ...... after time t_2

(c) $A + B + C + D \times t_3/t_4 + E \times t_3/t_5$ ....after time t_3

(d) $A + B + C + D + E \times t_4/t_5$ .... after time t_4

(e) $A + B + C + D + E$ .... after time t_5

or the change in the meniscus, say, during the time interval between t_4 and t_5 has been brought about by the settling of $E(1 - t_4/t_5)$. Similarly, the meniscus changes due to the settling of other particles are computed. Since the total change in the meniscus reading due to the settling of the whole suspension is known, the percentage of any fraction is easily calculated.

Times t_1, t_2, etc., corresponding to diameters d_1, d_2, etc., are calculated from Stokes' law, or may be taken from Table 1 given on page 231.

When the suspension has been settling for a few hours, and it is required to find the percentage of particles left in it, the instrument

is gently raised, after the two-way tap has been closed, by 1 or 2 cm and the change in the manometer noted after the connection has been established again.

$$\text{Since } D^2/d^2 \times (S-1)v/200 = a$$

where S is the density of the suspension, if now the instrument is raised by 1 cm, we have

$$D^2/d \times (S-1)(v-1)/200 = a'$$

and the change in the manometer reading being $a - a' = r$, we have

$$r = D^2/d^2 \; \frac{(S-1)v - (S-1)(v-1)}{200}$$

$$= D^2/d^2(S-1)/200 = \text{K } (S-1)$$

From this equation S can be calculated and being proportional to the concentration, the latter is easily known. In practice, the relation between $a-a'$ and S, or rather the concentration of the suspension, is worked out once for all as a part of the calibration of the instrument. Obviously this instrument can be used for finding the density of any liquid or suspension. Another point worthy of note is that in the equation given above it is assumed that the density of the suspension is the same within a vertical distance of 1 cm. Though it is true for distances of this order, it must be remembered that density changes in a vertical column of a settling suspension. This instrument enables us to determine the density gradient in a settling column.

Suppose, for instance, the density of the column at a level 1 cm higher than the previous level is S'; then the change in level of meniscus, say r', is given by the equation

$$r' - r = S' - S$$

Therefore if S, the density or concentration of suspension at depth v, is known, then the concentration at depth $(v-1)$, $(v-2)$, $(v-3)$....,etc., is easily found from the above relation. In other words, the change in reading for a 1-cm vertical shift of the manometer is constant if the density of the suspension is uniform, and any excess of density at one level over the other will be reflected in the departure from this reading. This method will prove very valuable for fine suspensions which may take several days to settle. The density gradient and consequently the size distribution of particles in such a suspension could easily be determined with this apparatus.

Directions for Filling the Instrument. The density of aniline-benzene mixture is adjusted with a hydrometer. This approximately

corresponds to 4 parts of aniline and one part of benzene. About 500 cc is prepared and stored for use. It is to be remembered, however, that since aniline-benzene mixture has a coefficient of expansion higher than water, the density should be adjusted whenever there is an appreciable rise or fall in the working temperature, especially the former.

The apparatus is thoroughly cleaned with H_2SO_4-chromic acid mixture before filling. This is done best by filling the manometer through the middle vertical tube with the cleaning mixture and leaving overnight. Next day, after thorough washing, the instrument is filled with water to which just enough NaOH has been added to make it alkaline to phenolphthalein. The vertical tube is then filled with the aniline-benzene mixture through the cup. The side tubes are then put into two cylinders filled with water to the same level and connected through the manometer by gently opening the tap connecting the vertical tube with the manometer.

When the necessary amount of the mixture has been let in, some mercury is poured into the vertical tube, and by again opening the tap gently it is allowed to rise about a centimeter above the tap. This mercury seal is necessary, as otherwise the aniline-benzene mixture dissolves the tap grease and slowly leaks out. The actual time required to fill the instrument after cleaning is not more than 10 to 15 minutes. The meniscus in the manometer should move up and down freely with an even convex curvature. Any tendency to stick or flatten at the interface is an indication that the instrument has not been cleaned properly.

Sometimes the aniline-benzene thread breaks or shows a tendency to break; in that case all of it is swept out by dipping one of the side tubes into a cylinder containing alkaline water and siphoning. Mercury is then poured out. Bubbles of air that collect in the spiral tube as a result of the pushing out of mercury are removed by siphoning out water and refilling the manometer as before. This emptying and refilling takes only five minutes at the most. The cylinders should be kept over a stone bench. Slight variations of temperature do not matter if they affect the two cylinders equally; but if one side faces a window, or the room is drafty, the results might be affected. In such cases the cylinders should be kept in bottomless wood cases or immersed in a tank of water.

CHAPTER IV

PIPETTE METHODS

The history of mechanical analysis of soils entered a new era with the development of what is known as the pipette method, independently discovered by Robinson in England, by Jennings, Thomas and Gardner in America, and by Krauss in Germany. Of these the Robinson technique is the simplest and is the one generally used for routine examination of soils. In its simplest form the apparatus consists of a glass cylinder or bottle of uniform diameter and a pipette with a long stem capable of drawing a sample of the suspension from any desired depth in a settling column. A slightly more elaborate arrangement which the author found useful for routine analyses and which could be fixed on a special bench reserved for the purpose, is described below:

A large aspirator bottle fitted with a manometer (Figure 2) is connected to a vacuum pump and a system of taps, by means of which the rate of filling the 50-cc pipette could be adjusted from 12 to 18 seconds, after which it is left in position, the pressure in the aspirator being noted.

It can then always be evacuated to the same extent, and the rate of sampling will be the same. By means of a small rubber bulb interposed between the pipette and the aspirator bottle, the excess on 50 cc of suspension can be pressed out when the sampling is completed.

The pipette, marked at a distance of 5, 10 and 20 cm from the tip, is first adjusted by means of a sliding clamp stand so that either one of the marks is at the same level as the suspension in the cylinder as seen from outside. It is then gently lowered into the suspension by lifting the clamp stand, when the tip goes down to the desired depth. The sample is taken by suddenly opening the tap (A) connecting the pipette with the aspirator, and closing the tap (D) when the suspension is just above the 50-cc mark. The pipette is then lifted and the suspension brought to the 50-cc mark by gently pressing the bulb, the excess flowing back into the bottle. The suspension is then emptied into a weighed beaker, dish, or conical flask, evaporated to dryness, and weighed. A special pipette with a two-way tap, which when filled can deliver the correct volume automatically by turning the tap, can be substituted for the ordinary

pipette with the rubber bulb. Though some workers use a 20-cc pipette, the author prefers a 50-cc pipette and 2 per cent suspension, so that the weight of the residue gives the percentage of the particular fraction by shifting the decimal place, i.e., multiplying with 100.

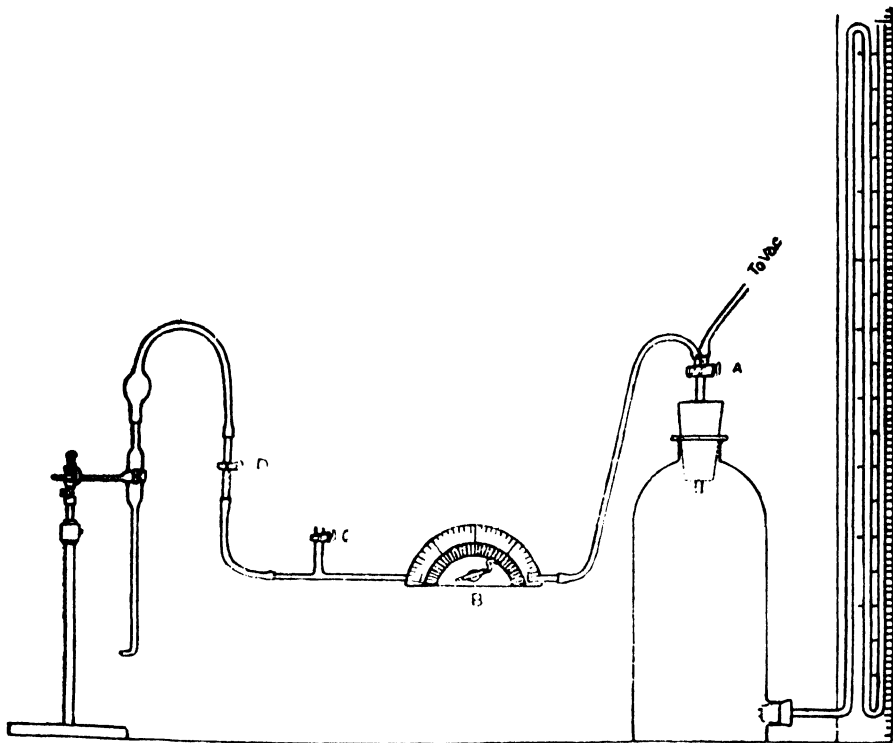



Fig. 2. Pipetting Apparatus

A weighed amount of air-dry soil (preferably passed through 1-mm mesh sieve) is suspended in enough water to give a 2% suspension on the oven-dry basis. This precaution is very often omitted by workers. All results of mechanical analysis must be recorded on the oven-dry basis and not on the air-dry basis, as the moisture contained in the soil is a very variable entity.

Having prepared a 2% suspension in distilled water, we proceed to determine the percentage of various fractions. There is no general agreement as to the size limits of the various fractions into which the soil particles are divided; it is very difficult to choose between the various groupings used in different countries, especially since all of them have been fixed arbitrarily. The use of summation curves, however, renders us independent of any system of particle grouping; moreover, it brings out the characteristic particle-size distribution of each soil much more clearly than a series of figures giving the percentage amount of each fraction present. For

the purpose of constructing summation curves, the author prefers to make use of the following grouping, which is at once the nearest approach to all the existing systems, thus facilitating interpolation to any of the prevalent systems, as the values to be determined would be very close to the experimental points on the curve.

Names and sizes of fractions obtained by mechanical analysis of soils

Name of particles		Limits of diameter of particles (mm)
Sand	Coarse sand	1 - 0.2
	Fine sand	0.2 - 0.05
	Very fine sand	0.05 - 0.02
Silt	Coarse silt	0.02 - 0.01
	Fine silt	0.01 - 0.005
	Very fine silt	0.005 - 0.002
Clay	Clay	0.002 - 0.001
	Ultra Clay	below 0.001

Suppose we start with a uniform 2% suspension of the soil, and the prevailing temperature is 15° C. The pipette method is not suitable for particles larger than 0.05 mm diameter. Therefore, we proceed to determine particles with a limiting diameter of 0.05 mm. From Table 1 (page 231) it will be seen that at 15° C particles 0.05 mm in diameter will have just reached the 10-cm depth in 51 seconds. During this time all the larger ones will have settled below this depth. If we start pipetting at this depth a few seconds earlier and finish a few seconds later to compensate for the time spent in filling the pipette, we shall have sampled an aliquot of that portion of the soil suspension which contains the same concentration of particles of 0.05 mm and below as was contained in the original suspension, to the exclusion of larger particles. If we evaporate this measured volume to dryness and weigh the residue we shall know the concentration of all particles up to the limiting diameter of 0.05 mm.

If we shake the suspension again and sample at 10 cm depth after allowing the suspension to settle for 319 seconds (see Table 1) we shall have eliminated all particles over 0.02 mm and collected all those having a diameter less than 0.02 mm. Similarly, by shaking the samples one after the other, allowing them to settle, and pipetting after 21.3 minutes, 85.1 minutes, 8.81 hours and 36.45 hours, particles of 0.01, 0.005, 0.002, and 0.001 mm diameter, respectively, could be sampled. In each successive sampling a portion of the coarser fractions is eliminated; the difference between any two

gives the percentage of any particular fraction. The method of plotting and interpolation will be discussed later.

It is obvious that sampling must be begun from the coarsest fraction, gradually eliminating them until the finest fraction determined is reached. It is not permissible to start with the finest fraction, as in that case the decrease in the volume of the suspension produced on drawing a particular sample will result in a change in the concentration of the coarser fractions. It might be mentioned that the time of settling can be fixed at any convenient figure by adjusting the depth of sampling to a corresponding degree. For coarser fractions a depth of 30 to 40 cm is more appropriate, and for clay a depth of 2.5 cm and even less gives results identical with greater depths. For coarser fractions the suspension may be transferred to a tall cylinder and depth of sampling increased, or these fractions may be separated by beaker method. If more detailed information about the coarser fractions is required, the use of the Puri Siltometer, to be described later, is advocated.

CHAPTER V

HYDROMETER METHOD

The use of the hydrometer for mechanical analysis of soils has been popularized by Bouyoucos. The method has been criticized by Keen. To overcome some of the objections to the ordinary design, a new type of hydrometer (Figure 3) which has a long, thin stem and a short bulb, records density changes in a column 8 to 10 cm long and situated 50 to 60 cm from the top, was devised by the author. The successful working of this hydrometer depends on the fact that the gradient of increasing density in the suspension of a sedimenting column becomes less and less steep as we go from top to bottom. In other words, the average density of a suspension, the length of which is small compared to the total depth of the sedimenting column, may be taken without serious error as the density of its middle point. This hydrometer gave results in close agreement with the pipette method. In practice, however, it has two drawbacks, namely, the difficulty of making a long stem stand upright, and the likelihood of breakage.

The hydrometer, though extensively used by road engineers, has never appealed to soil scientists as an instrument of precision which could replace the ordinary pipette method for routine laboratory analysis of soils.

One serious drawback in the hydrometer technique as compared to the pipette method is that the former does not measure the concentration of particles at one point, but rather gives the average density of a fairly large section of the sedimenting column. This section, moreover, is not situated at a fixed distance from the top, but moves with the changing concentration of the suspension, which affects the resting point of the hydrometer. The first defect is fundamental; it cannot be overcome unless a point hydrometer can be produced, or the concentration gradients in sedimenting columns can be examined and the magnitude of the errors involved shown to be insignificant. The second defect could be obviated by the use of a constant-immersion hydrometer.

The basis of the hydrometer method rests on a single assumption: namely, that the average density of any section of a sedimenting column is equal to the density at its middle point. Curiously, this assumption has never been subjected to a rigid test, though general agreement between the hydrometer and the pipette methods has been

shown; it has been ascribed largely to compensating errors assumed to have been operative in the majority of cases. This leaves the theoretical background unsound and consequently the element of doubt has persisted.

Complete summation curves of 150 soils were determined by the pipette method. Ten-, 15-, and 10-cm sections of the settling column, commencing from a depth of 5 cm from the surface, were considered as representing the lengths of the hydrometer stem. The

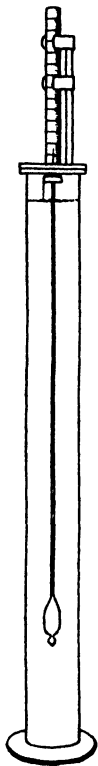



Fig. 3. Diagram of the New Type of Hydrometer and Reading Device

percentage of particles corresponding to each of several different times at the middle point of the section was determined by interpolation from the summation curves and calculated by taking the mean of percentages at the two extremities of this section. It was argued that if these two sets of values were similar, the soundness of the assumption that the mean density equals the density at the middle of any section would be established. Further, the limiting length of the hydrometer bulb within which this relation holds would also be known. The absolute difference between the percentage of particles calculated from the mean density and that determined directly at the middle point for various sizes, is given in Table 2, against the percentage of the total number of soils showing this difference.

Table 2.

Comparison of percentages of particles calculated from the mean densities of sections of settling columns with those from densities at their middle points

Limiting sizes of particles mm.	0.05			0.02			0.01			0.005			0.002		
Length of hydrometer bulb.....cm.	10	15*	20*	10	15	20	10	15	20	10	15	20	10	15	20
Difference between percentage found by two methods				Percentage of soils											
10	0	2.1	4.2	0	0	0	0	0	0	0	0	0.7	0	0	0
9	0	2.1	2.1	0	0	0	0	0	0	0	0	0	0	0	0
8	0.7	0	2.1	0	0	0	0	0	0	0	0	0	0	0	0
7	0	0	4.2	0	0.7	2.0	0	0	0	0	0	0	0	0	0
6	0	2.1	2.1	0	0	0.7	0	0	2.7	0	0	1.3	0	0	0
5	0.7	4.2	6.3	0	2.6	3.3	0	0.7	1.3	0	0.7	1.3	0	0	0
4	0.7	6.3	2.1	0.7	2.1	6.7	0	0.7	4.0	0	2.0	2.7	0	0	0
3	2.0	10.4	10.4	3.3	8.7	17.3	0.7	3.3	7.3	0	3.3	3.3	0	0	2.1
2	12.6	16.7	22.9	14.0	24.6	22.7	4.0	17.3	23.7	4.6	9.3	16.7	0	0	0
1	39.3	31.3	25.0	36.6	36.7	30.7	22.0	44.0	34.0	21.3	30.7	30.7	0	0	14.6
0.5 and less	44.0	25.0	18.0	45.4	24.6	16.7	73.3	34.0	26.0	74.1	54.0	44.0	100.0	100.0	83.3

*48 samples only, for each of these lengths, were analyzed for this size.

It will be seen that in all cases the density gradient for any column below a depth of 5 cm is symmetrical, and that, therefore, the density at its middle point is equal to the mean of the densities at the extremities. The differences increase as the bulb of the hydrometer is made longer, but only in the case of coarser fractions. For clay fractions, the bulb may be as long as 20 cm without introducing any appreciable error. We are therefore justified in taking the average density of any column and assuming it to be equal to the density at its middle point.

This conclusion is of great importance and must set at rest any misgiving regarding the use of the hydrometer for the mechanical analysis of soils and the acceptance of such results as truly representing the size distribution of particles. It must be admitted that there is no theoretical reason why the density gradients of sections of sedimenting columns of soils should show such symmetry, but there is also none why they should not: therefore, facts must be accepted as they are. This fundamental fact having been established, attention was directed to the design of a constant-immersion hydrometer specially suited to the measurement of density of suspensions. This resulted in the design of the Chaino-hydrometer which has placed the hydrometer method of mechanical analysis on a theoretically sound basis and has imparted to the whole procedure the precision of theory and experiment associated with the science of pure physics.

The Chaino-Hydrometer

It is well known that measurements of weight can be made with far greater precision than those of volume. It is for this reason that the analytical balance has never been surpassed for measuring the densities of liquids and that the hydrometer has been accepted as a rough and ready method only on account of the great saving in time. The design of the Chaino-hydrometer resulted from the attempt to combine the rapidity of the hydrometer and the precision of the analytical balance. It has proved to be an extremely sensitive instrument for measuring the densities of liquids, especially soil suspensions.

The Chaino-hydrometer, the principle of which is embodied in the well known Nicholson hydrometer, is shown in Figure 4. It is made of brass and is chromium-plated. Its stem is shaped from a steel knitting needle. The attached needle point indicates the limit to which the hydrometer is to be immersed; with this device the immersion can be reproduced to a fraction of a millimeter. On top of the stem is fixed a Bakelite tube and a hook. A fine chain 25 cm long and weighing 0.5 gm passes through the tube, forms a loop, and ends on the hook on the hydrometer stem. The chain hangs from a hook fixed on a rack and pinion which can be raised or lowered by a thumb screw against a vernier scale. A movement of 1.6 cm on the scale corresponds to a change of 10 milligrams in

the weight of the hydrometer. A total weight of 100 milligrams could be added by the Chaino-metric arrangement. Larger weights are added directly on the special hooks fixed on the stem.

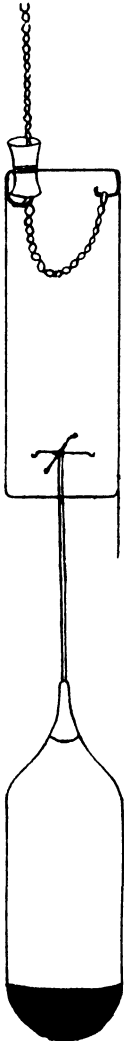
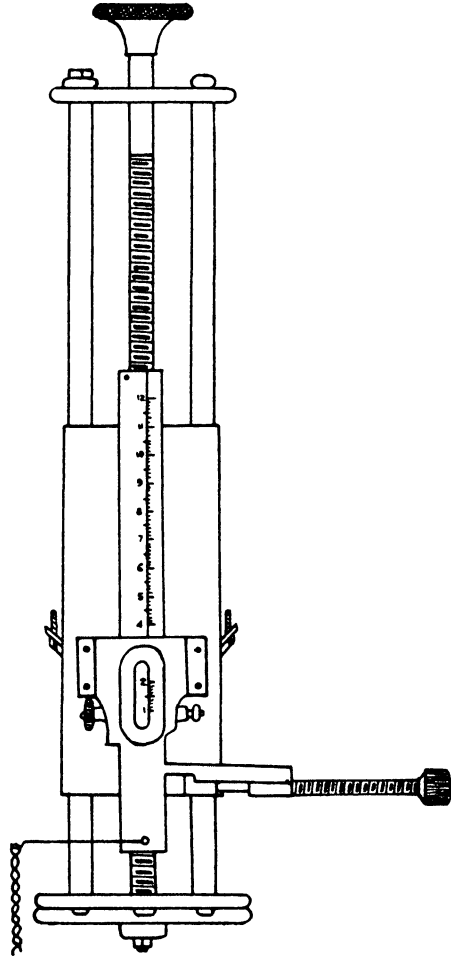



Fig. 4. Diagram of the Chaino-hydrometer

For uniformity of results, the chain must have a fixed initial loop when the vernier registers zero. This is accomplished by the help of another screw, shown at the top, which can move the whole Chaino-metric arrangement. This is worked until a fixed number of chain rings or a fine mark on the chain has passed across a pointer.

From this point onward the vernier scale is manipulated until the needle touches the surface of the liquid, when the hydrometer registers the true density of the suspension. It is important that the initial loop of the chain be made immediately before a reading is taken, and the final reading should always include a loop which is bigger than the initial one.

Hydrometers can be easily made from the bulbs of 100-cc and 50-cc pipettes, by sealing both ends and attaching the steel needle stem with sealing wax. If such a hydrometer breaks, a new one can be constructed ready for use within a few hours. The brass ones are, however, preferable. The glass hydrometers are weighted with mercury and the brass ones with lead shot.

Temperature Correction

For a sensitive hydrometer, temperature correction is absolutely essential. This is calculated by weighing the hydrometer and taking into consideration the fact that all of that weight is lost when the hydrometer floats freely in water. The volume of the immersed portion of the hydrometer is obtained from the volume of an equal mass of water at that temperature. Knowing the coefficient of expansion of water with temperature, a table can be constructed which will give at a glance the weight of the hydrometer in water at all temperatures. Thus if W is the weight of the hydrometer and W_t the additional weight added to bring it to the constant-immersion point at room temperature t, then

$$W + W_t = v \times d_t$$

where v is the volume of the immersed portion of the hydrometer and d_t the density of the water at any temperature t. The values of the additional weight at other temperatures are calculated from the known values of the density of water at these temperatures. In this relation it is assumed that v, the volume of the hydrometer, remains constant. Since the hydrometer is extremely sensitive, the results are affected by the expansion or contraction of the material forming the bulb, and a positive or negative correction has to be applied when constructing the temperature-correction chart.

If V_t is the volume of the hydrometer at temperature t, then volume at any other temperature, t', is given by the formula

$$V_{t'} = V_t\left[1 + \tau\,(t' - t)\right]$$

where τ is the coefficient of cubical expansion of the material forming the hydrometer. Thus the complete temperature-correction chart can be constructed from the formula

$$W + W_t = V_t \times d_t$$

Thus a single weighing to find W and a single reading at any temperature t to find W_t suffices to construct the complete temperature-correction chart. Actually the values of W_t are taken at three or four temperatures to check the calculated and found values. The values of W_t need not be calculated for fractions of a degree; this can be done for whole numbers, and the results plotted on an open scale from which the intermediate values for fractions of a degree are interpolated when preparing the temperature-correction chart. Evidently the temperature-correction chart gives the change in the density of water in terms of W_t. It is also known that a change of density of 0.001 from that of water would produce a change of 0.001 $\times$ v gm. in W, where v is the volume of the hydrometer. Thus if the volume of the hydrometer is 100 cc and if with the help of the chainometric arrangement W could be determined to within a milligram, the densities could be found correct to the fifth decimal place.

Actually an accuracy of this order is not necessary for the mechanical analysis of soils. The excess of density of a 1% suspension over water at the same temperature is 0.006269, assuming a density of 2.68 for the soil particles. This will produce a change of 0.006269 $\times$ V gm. in the weight of the hydrometer. Thus the percentage of particles of any fraction in a 1% suspension of soil is equal to:

$$\frac{(W' - W) \times 100}{V \times 0.006269}$$

where W' is the additional weight of the suspension at the constant-immersion point and W that of water at the same temperature (given in the temperature-correction chart). As V is constant, the multiplying factor is calculated only once. Strictly speaking, V changes slightly with temperature, but this change is negligible for this purpose and need not be considered. It will be seen that if V is made equal to 159.5 cc the multiplying factor becomes equal to 100 and $(W' - W)$ in centigrams gives directly the percentage of any fraction for a 1% suspension. Alternately, if the concentration of the suspension is made equal to $159.5/V$% the multiplying factor will be 100.

A hydrometer may be tested occasionally at room temperature in distilled water, and if any change in the weight (W) is observed a positive or negative correction is applied to all the values in the temperature-calibration chart.

It is worthy of note that the hydrometer gives the density of the suspension, whereas the pipette method gives directly the percentage of suspended matter by weight. Agreement between the two methods can be expected only if the density of different soils is the same. A density of 2.68 has been assumed for all soils. This value was obtained by actual measurements of density in a number of mineral soils; the average density was found to be 2.68, the lowest value

being 2.64 and the highest 2.71. It might be mentioned that a variation of 0.04 in the actual density of the soil from the mean value will produce a difference of 1% in the weight of the fraction. Since most of the mineral soils approximate this mean value the difference between the hydrometer and the pipette methods is not likely to be serious on this account.

An important consideration that arises in the use of the hydrometer is the disturbance likely to be caused by the insertion of a large body in a settling column. How far this may affect the accuracy of results can be determined only by a direct comparison of the hydrometer and the pipette methods. Sixty-one soils were analyzed by the two methods. The results are given in Table 3.

Table 3. Comparison between the hydrometer and the pipette method for determining percentages of fractions

Limiting size of particles (mm.)	0.02	0.01	0.005	0.002
Difference between percentages found by two methods	Number of soils			
4	3	1	1	0
3	3	2	2	0
2	10	7	9	4
1	13	19	22	12
0.5 and less	32	32	27	42

The absolute differences in the percentages of various fractions are given against the number of soils showing a difference of that order. The agreement is very good, in view of the fact that even in the pipette method a difference of the order of 2 in the percentage of any one fraction is within the experimental error of the instrument.

Reproducibility of results by the hydrometer was compared with that by the pipette method by analyzing fourteen soils five times by both methods. It was found that the reproducibility of results was actually better with the hydrometer method than with the pipette method.

It might be pointed out that there is nothing arbitrary or empirical in the use of the Chaino-hydrometer. The settling times of the particles of various sizes are calculated from Stokes' law to a depth corresponding to the middle point of the hydrometer bulb, which must be symmetrical about the axis. The hydrometer is lowered in the suspension just before the calculated settling time for the settling depth, corresponding to the middle point of the bulb of the hydrometer, just as the pipette is lowered in the pipette method. The disturbance caused is negligible, being no more than in the pipette method. The hydrometer is not recommended for continuous reading by keeping it in the suspension and taking observations at

definite intervals of time. Apart from the errors introduced by the actual settling of the particles on the bulb of the hydrometer, such a procedure would require a separate hydrometer for each suspension, and thus a number of soils could not be examined simultaneously without adding to the cost of equipment. The chainometric arrangement can be mounted on a robust stand that can slide between rails. The 1- or 2-liter cylinders containing the soil suspensions are arranged in a row, and the chainometric arrangement is brought behind each cylinder one after the other at the appropriate time.

After a rigid and exhaustive comparison of the two methods the pipette method has been replaced by the Chaino-hydrometer in the author's laboratory. It is found that complete mechanical analysis of the soil can be made in the time formerly required for determining the clay fraction only by the pipette method. The saving effected is not only in time but in the cost of equipment for dishes and heaters, which is considerable. With the Chaino-hydrometer one worker can complete the mechanical analysis of twenty soils in a day. If bench space is available for arranging cylinders in rows, it is not impossible to complete as many as 50 mechanical analyses in a day. The Chaino-hydrometer is by far the quickest of all the precision methods of mechanical analysis of soil, the pipette method being second.

CHAPTER VI

ULTRA-MECHANICAL ANALYSIS OF SOILS

The usual methods of mechanical analysis of soil, including the hydrometer and the pipette methods, have often been used for particles down to 0.001 mm in diameter. This size is larger than the upper limit of colloidal particles, which is 0.0005 mm. It is, however, possible to push the mechanical analysis to this extreme limit by gravity sedimentation by extending the time to several weeks. The use of the centrifuge in accelerating sedimentation would at once suggest itself. For ordinary mechanical analysis it was used to some extent before the pipette method had gained its popularity.

The modification of the pipette method to include a sedimentation tube which may be centrifuged is not possible. The reason is not far to seek; the pipette method is based on the assumption that all particles of the same size settle with the same velocity at all depths. While this is true for gravity settling, it is not true for sedimentation in a centrifugal tube, for the settling velocity of the particles is proportional to their distances from the axis of rotation. One way of overcoming this difficulty would be to make the length of the sedimenting column small compared to its distance from the axis of rotation. This would mean that if the sedimenting tube is 10 cm long, the axis of rotation should be at least 100 cm from the bottom of the tube. Although it is not impossible to construct a centrifugal machine with a span of 2 meters, the instrument could hardly be accommodated on a laboratory bench. As such an instrument might have to run for several hours, the vibrations and noise would necessitate its being housed in a special room.

Marshall has tried to overcome this limitation by putting a thin layer of soil suspension, from which all the coarser particles had been removed, on top of a thick layer of a denser liquid, such as sugar or a urea solution, and centrifuging this. Under these conditions, according to Marshall, the soil particles reaching the bottom of the tube after a given time are of about the same size.

The simplicity of gravity sedimentation and the application of the pipette method to the ultra-mechanical analysis of soils, though pointed out by Robinson, has so far escaped attention on account of the long settling time. If this could be shortened, the technique would be ideal, but it is possible only by reducing the depth at which

pipetting is done. Hitherto it has not been found practicable to have it less than 2.5 cm, but there seems no reason why it could not be reduced to 0.5 cm or even 0.1 cm. The actual pipetting could be so refined that only the top millimeters of the surface are removed. This would reduce the time factor considerably. For instance, we could catch particles of 40-mμ (0.00004 mm) diameter by pipetting at 1 mm after one week's settling, which would normally have taken 50 weeks if the pipetting was done at the customary 5-cm depth. The equivalence of the time/depth ratio has been shown for clay up to 2.5 cm, but smaller depths have not been attempted with the ordinary pipetting technique. The author has designed a micro-pipette for ultra-mechanical analysis. This instrument has been successfully used for pipetting at extremely small depths, and with its help the equivalence of the time/depth ratio has been established down to 1-mm depth.

Description of the Apparatus

The micro-pipette consists of a 10-cc pipette with a hypodermic needle attached to the tip. The pipette is provided with a two-way tap at the suction end so that when it is closed the pipette holds exactly 10 cc of the suspension, the excess flowing out at the other end of the tap. It is mounted on a rack-and-pinion stand capable of controlled movement to the fraction of a millimeter. The pipette can be moved by two screws, one of which causes it to move against a graduated scale with vernier attachment. The pipette is first moved down with one screw until the tip of the hypodermic needle just touches the surface of the suspension. This point is extremely sharp and can be reproduced to the fraction of a millimeter. From this point the second screw is rotated and with the help of the vernier scale the tip of the needle is accurately let down to any desired depth. The suction is applied with the help of a mercury reservoir attached to a bulb, which is alternately filled and emptied by raising or lowering the reservoir. The rate at which the pipette is filled is controlled by the tap leading to the reservoir.

When the pipetting is complete, the mercury pressure is relieved by raising the reservoir and the pipette emptied by detaching the hypodermic needle and thus widening the opening. The pipette is first calibrated to deliver exactly 10 cc, which is quite enough for evaporating to dryness in a crucible and weighing the residue. A hypodermic needle can be joined directly to a 10-cc pipette with its tip filed off. There is sometimes air leakage at the ground-on joint between the hypodermic needle and the tip of the syringe, but it gives no trouble if it is kept well greased. When it shows signs of wear, it should be replaced by a new syringe.

As we are concerned only with the top portion of the liquid at no great depth, the use of tall sedimenting cylinders is obviously not appropriate. Squat bottles, which are wide but not too tall are used for holding the suspension. If the diameter of the bottle is 16 cm

the removal of 10 cc of the suspension by pipetting makes a difference of only 0.5 mm in the height of the liquid.

It might be mentioned that the tip of the hypodermic needle has a nib-shaped point which is rather an advantage as the suction creates horizontal stream lines and the disturbance is minimal. It must be remembered, however, that the actual opening is above the tip and allowance should be made for this distance in letting down the tip to the proper depth at the time of sampling.

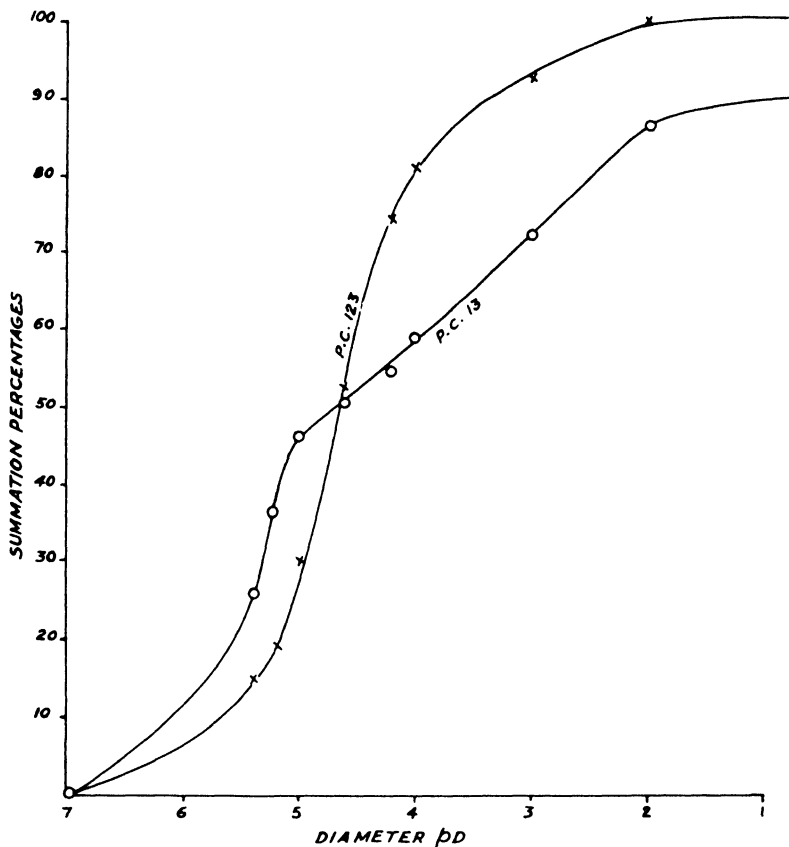



Fig. 5. Summation Curves of Two Soils (P.C. 13 and P.C. 123)

Settling Rate of Particles

Typical summation curves illustrating the ultra-mechanical analyses of two soils of entirely different types are given in Figure 5. When dealing with particles of colloidal dimensions in the region of the ultra-clays, it is necessary to use the logarithmic scale, and the diameter of the particles may be expressed in terms of the negative index of 10, just as in the pH scale of expressing acidity or alkalinity, or the pF scale expressing soil moisture. The diameter of the particles is then referred to as pD, where *D* is the particle diameter in centimeters. The curves in Figure 5 have been plotted

on this basis. There are other advantages of adopting this scale, which will be explained later.

The time taken by particles of various sizes below 0.001 mm to settle to a depth of 1 cm from the surface at various temperatures

Table 4. Showing the time of fall of particles of various diameters in water at different temperatures through a depth of one centimeter

Time of fall through a depth of 1 cm. of various size

Temp. °C	.001 mm. 10^{-4}cm. (pD=4.0) Hrs. Min.	.000631 mm. $10^{-4.2}$cm. (pD=4.2) Hrs. Min.	.000398 mm. $10^{-4.4}$cm. (pD=4.4) Hrs. Min.	.000251 mm. $10^{-4.6}$cm. (pD=4.6) Hrs. Mins.	.0001585 mm. $10^{-4.8}$cm. (pD=4.8) Hrs. Mins.
10	3-58	9-58	25- 2	62-53	157-57
11	3-51	9-41	24-20	61- 8	153-33
12	3-45	9-25	23-40	59-27	149-19
13	3-39	9-10	23- 1	57-50	145-16
14	3-33	8-55	22-25	56-18	141-25
15	3-28	8-41	21-50	54-50	137-44
16	3-22	8-28	21-16	53-25	134-12
17	3-17	8-15	20-44	52- 4	130-47
18	3-12	8- 3	20-13	50-46	127-32
19	3- 7	7-51	19-43	49-31	124-24
20	3- 3	7-40	19-14	48-19	121-23
21	2-59	7-29	18-47	47-10	118-29
22	2-54	7-18	18-20	46- 3	115-42
23	2-50	7- 8	17-55	45- 0	113- 1
24	2-46	6-58	17-30	43-57	110-25
25	2-43	6-49	17- 6	42-58	107-56
26	2-39	6-40	16-43	42- 1	105-32
27	2-36	6-31	16-21	41- 5	103-13
28	2-32	6-22	16- 0	40-12	100-58
29	2-29	6-14	15-39	39-20	98-48
30	2-26	6- 6	15-20	38-30	96-42
31	2-23	5-58	15- 0	37-42	94-42
32	2-20	5-51	14-42	36-55	92-45
33	2-17	5-44	14-24	36-10	90-52
34	2-14	5-37	14- 7	35-27	89- 2
35	2-12	5-30	13-50	34-44	87-16
36	2- 9	5-24	13-34	34- 4	85-34
37	2- 6	5-18	13-18	33-24	83-54
38	2- 4	5-12	13- 3	32-46	82-18
39	2- 2	5- 6	12-48	32- 9	80-45
40	1-59	5- 0	12-33	31-33	79-14

is given in Table 4. These have been calculated from Stokes' law. Times of fall of particles of $10^{-5.0}$, $10^{-5.2}$, $10^{-5.4}$, $10^{-5.6}$, $10^{-5.8}$ and $10^{-6.0}$ cm diameters may be found by multiplying the times of fall of particles of $10^{-4.0}$, $10^{-4.2}$, $10^{-4.4}$, $10^{-4.6}$, $10^{-4.8}$ and $10^{-5.0}$ cm diameter by 100, respectively. Remembering that the equivalence of time/depth ratio holds even to 1 mm depth, the time of settling for any depth can be easily calculated.

The micro-pipette method is simple, straightforward and theoretically as sound as the well known pipette method. A dozen or

more samples can be started at the same time, put aside for settling, and pipetted one after the other at appropriate depth/time intervals. The diameters are taken corresponding to $10^{-4.0}$, $10^{-4.2}$, $10^{-4.6}$, $10^{-5.0}$, $10^{-5.2}$ and $10^{-5.4}$. The lowest diameter is thus 0.0000398 mm, i.e., a little less than 40 mμ. This size would take little more than seven days to settle through 1 mm depth at 25°C. It is convenient to determine particles corresponding to $10^{-4.6}$, $10^{-4.2}$ and $10^{-4.0}$ by allowing the suspension (at 25° C) to settle for 5 hours and 25 minutes and pipetting off at 1.25-mm, 8.0-mm and 2-cm depths. The suspension is again shaken and left for 7 days and 3 hours and then pipetted at 1 mm, 2.5 mm, and 6.3 mm to determine particles corresponding to D $10^{-5.4}$, $10^{-5.2}$ and $10^{-5.0}$

CHAPTER VII

SILTOMETER FOR THE MECHANICAL ANALYSIS OF SANDS AND SILTS

The limiting diameters of particles that can be conveniently analyzed mechanically by the pipette method are of the order of 0.05 mm; by means of a long cylinder the upper limit could be pushed to 0.1 mm. Beyond that it is not possible to go on account of the extremely rapid rate of fall of these particles. Theoretically it is possible to use a liquid with greater viscosity, but the procedure would be very cumbersome. The use of sieves, though convenient, leaves much to be desired. Apart from the fact that a change from settling in water to measurement by passing through a narrow opening would leave a gap of considerable magnitude, the range of sieves available is not sufficiently precise to admit interpolation to intermediate values. Two precise instruments for the mechanical analysis of silts are:

(a) the optical lever siltometer of Vaidianathan

(b) the Puri siltometer.

The optical lever siltometer is based on the same principle as the manometric sedimentation method of Wiegner referred to previously, with the difference that the pressure changes are measured with a mercury manometer, connected with an optical lever to magnify the movement of mercury. The siltometer consists of a long tube into which the silt is dropped, pressure changes during settling being recorded by the optical lever on a revolving photographic plate. The instrument is extremely sensitive and accurate but requires elaborate apparatus and demands skilled handling.

The Puri siltometer is based on the principle of grading silt particles by allowing them to fall through a long column of water and collecting the different fractions in separate boxes that move into position under water at predetermined intervals of time. The siltometer shown in Figure 6 consists of three parts.

(a) The siltometer tube

(b) Silt-dropping device

(c) Silt-collecting arrangement.

(a) The Siltometer Tube. This is a 200-cm brass tube of 2.5 cm internal diameter. It is carried on a lever mounted on a fixed axis. With this lever the tube can be raised or lowered through a distance

of about 1 cm. The last half inch of the tube is tapered so that the diameter of the lower end is about 1.5 inches.

(b) Silt-dropping Device. When silt is dropped in water in the dry condition, it carries down with it entrapped air which is dislodged gradually and then rises to the surface in the form of tiny

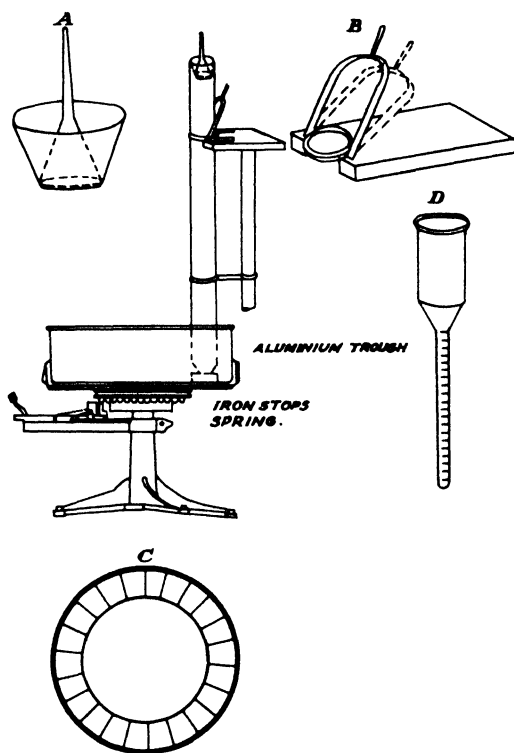



Fig. 6. Siltometer

bubbles. This phenomenon can be watched by dropping silt in a glass tube filled with water. By means of the dropping device used with this instrument, silt is dropped under water in the wet condition, which renders the distribution of particles uniform and their downward movement regular. The device shown diagrammatically in Figure 6 consists of a glass or metal funnel into which another inverted funnel fits so as to be water-tight. The silt is placed around the inner funnel and the whole arrangement placed on the top of the siltometer tube which is filled with water. When all is ready, the inner funnel is lifted and a stop-watch is started at the same time. The other funnel is then lifted and the top of the siltometer tube closed by placing a rubber bung on it.

(c) Silt-collecting Arrangement. The silt-collecting arrangement consists of a circular aluminum trough with twenty boxes arranged around its circumference. The trough is mounted on a turn-table

having twenty iron stops arranged in a circle at equal distances. Each one of these iron stops in turn rests against a wedge-shaped piece of iron. The turn-table is rotated by a spring fixed to its base. The stop is released by pushing forward a lever which also operates a second wedge to arrest the movement of the trough by coming against the second stop. The lever returns to its original position along with the second wedge when released, bringing the second wedge against the second stop. In this way the trough can be moved one-twentieth of its circumference at each operation of the lever, thereby causing the different collecting boxes to rotate into position in sequence. The lever is pressed at definite intervals of time. These are given in Table 5 together with the corresponding diameters of the particles for various temperatures of sedimentation.

It might be noted that Stokes' law is not strictly applicable to coarser particles and for accurate results the calculated diameter must be multiplied with what is known as Zahm's multiplying factor. The values in Table 5 were calculated as follows:

The starting point of the calculation is the familiar Stokes' formula for the velocity of spherical bodies moving under gravity through a fluid, viz.,

$$V = 2/9 \frac{-gr^2 (\rho - \sigma)}{\eta}$$

where V = velocity of the falling particles if t is the time of fall = $200/t$

g = Acceleration of gravity = 981 cm/sec^2
ρ = Average density of silt particles, assumed as 2.65
σ = Density of water = 1.00
η = Viscosity of water at the temperature of the experiment.*

This on reduction, gave for a Siltometer of length 200 cm

$$d^2 = \frac{800}{359.7} \cdot \frac{\eta}{t}$$

whence d (Stokes' diameter) was evaluated for various times of fall, at various temperatures.

Next the constant R (Reynolds number) was evaluated for each value of d by the formula:

$$R = \frac{Vd\sigma}{\eta} = \frac{200d}{\eta t}$$

where V = Velocity as above = $200/t$
d = Stokes' diameter

σ = Density of water = 1.00
η = Viscosity as above.

Zahm's multiplying factor was next interpolated for each value of R from a table which gave its values for only certain fixed values of R.

The product of the corresponding values of "Stokes' diameter" and "the multiplying factor" is the "equivalent diameter of the falling particles".

Working Details. The trough is filled with water to a depth of about 3 or 4 inches and the collecting boxes arranged in position. One of the collecting boxes has a rubber bung lying in it. The siltometer tube is allowed to rest on this bung, thus closing the lower end effectively. The tube is then filled with water and about 10 grams of silt dropped in by the dropping device. A stop-watch is started simultaneously and the top of the siltometer tube closed by placing a large rubber bung on it. The tube is then raised by the lever, which results in its being opened at the bottom. The collecting trough is moved by one notch, which brings the first box underneath the tube. The lever is pressed after 26 seconds and then after every 4 seconds up to 66 seconds; and then after 136, 166, 196, 376 and 556 seconds. The last time interval gives particles of about 0.06 mm diameter. It is not necessary to fractionate particles of smaller diameter than 0.06 mm, which are rarely present in appreciable quantity in silts and which can be separated from the silt sample by ordinary sedimentation before analyzing in the siltometer. The horizontal column in Table 5, corresponding to the temperature of the water in the siltometer, gives the reduced diameter in mm of silt particles collected in the different boxes. The various fractions are emptied out of the boxes onto filter papers (Whatman 50) and dried for a couple of hours in a steam oven, after which they are weighed on a torsion balance.

Another method of measuring the quantity of each fraction is to take its volume in a graduated tube. For this purpose, the silt is transferred in the wet condition and its volume taken under water, in special measuring tubes (Figure 6D). If the volumes of the various fractions are added and the volume of each fraction is reckoned as a percentage of the total volume, we get results which are in close agreement with those found by drying and weighing the fractions. Silt particles move quite freely under water and there is no difficulty in measuring the volumes accurately in narrow graduated tubes, provided the particles are more than 0.06 mm in diameter. In the laboratory, however, where drying arrangements and a torsion balance for rapid weighing are available, it is quicker to use the weighing method, especially as the time taken in drying is not counted as spent in work and two men can speed up the work by a division of labor.

TABLE 5. Showing the reduced diameter in mm. of silt particles settling through a vertical water column 200 cms. long in various times and at different temperatures

Temp. °C	Time in seconds																			
	26	30	34	38	42	46	50	54	58	62	66	76	86	96	106	136	166	196	376	556
10	.618	.541	.483	.438	.401	.371	.344	.325	.307	.291	.277	.249	.227	.209	.195	.165	.146	.131	.091	.074
11	.612	.536	.478	.433	.397	.367	.342	.321	.303	.287	.274	.246	.224	.207	.193	.163	.144	.130	.090	.073
12	.606	.530	.473	.429	.393	.363	.339	.317	.300	.284	.271	.243	.221	.204	.190	.161	.142	.128	.088	.072
13	.600	.525	.468	.427	.389	.360	.335	.314	.297	.281	.268	.240	.219	.202	.188	.159	.140	.126	.087	.071
14	.594	.520	.464	.421	.385	.356	.332	.311	.294	.278	.265	.237	.217	.200	.186	.157	.138	.125	.086	.070
15	.588	.515	.459	.416	.381	.352	.328	.308	.290	.275	.262	.235	.214	.198	.184	.155	.137	.123	.085	.069
16	.583	.510	.455	.412	.378	.349	.325	.305	.287	.272	.259	.232	.212	.196	.182	.153	.135	.122	.084	.068
17	.577	.505	.451	.408	.374	.346	.322	.302	.285	.270	.256	.230	.209	.193	.180	.152	.134	.120	.083	.067
18	.572	.501	.446	.404	.370	.342	.319	.299	.282	.267	.254	.228	.207	.191	.178	.150	.132	.119	.082	.066
19	.567	.496	.443	.400	.367	.339	.315	.296	.279	.264	.251	.225	.205	.189	.176	.148	.130	.118	.081	.066
20	.562	.492	.438	.397	.363	.336	.312	.293	.276	.262	.249	.223	.203	.187	.174	.147	.129	.116	.080	.065
21	.557	.487	.435	.393	.360	.333	.310	.290	.274	.259	.246	.221	.201	.185	.172	.145	.127	.115	.079	.064
22	.553	.484	.431	.390	.357	.330	.307	.288	.271	.257	.244	.219	.199	.183	.171	.144	.126	.114	.078	.063
23	.548	.480	.428	.386	.354	.327	.304	.285	.268	.254	.242	.217	.197	.182	.169	.142	.125	.113	.077	.063
24	.544	.476	.424	.383	.351	.324	.302	.282	.266	.252	.240	.215	.195	.180	.167	.141	.124	.112	.076	.062
25	.540	.472	.421	.380	.348	.321	.299	.280	.264	.250	.237	.213	.194	.178	.166	.139	.122	.110	.076	.061
26	.535	.468	.417	.377	.345	.319	.296	.278	.261	.247	.235	.211	.192	.177	.164	.138	.121	.109	.075	.060
27	.531	.465	.414	.374	.342	.316	.294	.275	.259	.245	.233	.209	.190	.175	.163	.136	.120	.108	.074	.060
28	.527	.461	.411	.371	.339	.313	.291	.273	.257	.243	.231	.207	.188	.173	.161	.135	.119	.107	.073	.059
29	.522	.458	.407	.368	.337	.311	.289	.271	.255	.241	.229	.205	.186	.172	.160	.134	.118	.106	.072	.059
30	.518	.454	.404	.365	.334	.308	.287	.267	.253	.239	.227	.203	.185	.170	.158	.133	.116	.105	.072	.058
31	.515	.451	.401	.362	.331	.306	.284	.266	.251	.237	.225	.202	.183	.169	.157	.131	.115	.104	.071	.057
32	.511	.447	.398	.359	.329	.304	.282	.264	.249	.235	.224	.200	.182	.167	.156	.130	.114	.103	.070	.057
33	.507	.444	.395	.357	.326	.301	.280	.262	.247	.233	.222	.198	.180	.166	.154	.129	.113	.102	.070	.056
34	.503	.441	.392	.354	.324	.299	.278	.260	.245	.231	.220	.197	.179	.164	.153	.128	.112	.101	.069	.056
35	.500	.437	.389	.351	.321	.297	.276	.258	.243	.230	.218	.195	.177	.163	.151	.127	.111	.100	.068	.055

CHAPTER VIII

METHODS OF CALCULATION AND GRAPHIC REPRESENTATION OF RESULTS OF MECHANICAL ANALYSIS

In the early days of mechanical analysis, the various soil fractions were designated as clay, silt and sand; by such adjectives as "fine" and "coarse", the range was extended to include about half a dozen fractions. The limiting diameters of the various fractions were fixed arbitrarily and depended on the whim of the individual worker. With the development of the mathematical theory of sedimentation by Odên and the introduction of the automatic balance, which was capable of resolving soil into almost innumerable fractions, the need arose for the representation of the data in the form of a continuous curve. Two graphic methods are available for this purpose; summation or accumulation curves and size-distribution curves. In summation curves the percentage of the various fractions obtained by weight are plotted as summation percentages against the limiting diameters; from the summation curve the values for the distribution curve are interpolated by readings at regular increments of diameter.

An example of mechanical analysis of an actual silt sample in the Puri siltometer will make the various steps clear. A silt sample from the bed of a canal was dropped in the siltometer tube at 28°C. The various steps in the calculation of values for distribution curve are given in Table 6. The summation curve is plotted in Figure 7 and the distribution curve in Figure 8.

Figure 9 shows some typical distribution curves of silts generally found in the bed of irrigation canals. It will be seen that the total range of particles lies between 0.06 and 0.6 mm - a very small range indeed as compared to soil in which the total range is of the order of from 0.001 to 1 mm. Whereas 100 divisions of a scale would accommodate all the various sizes in the case of silts, 1000 divisions are required for soils. Thus we shall be hard-pressed to find a graph-paper to accommodate all the sizes in one continuous curve. In the case of soils, therefore, we plot the logarithm of the diameter of the particles against their summation percentages.

Size-distribution curves of soils afford the most comprehensive picture of the mechanical composition of such aggregates. These curves, though characteristic of different soils, are not convenient for defining soils for purposes of classification. An attempt was

Table 6. Showing the various steps in the calculation of values for distribution curve of silt samples

Actual values				Interpolated values			
Time intervals sec.	Corresponding diameters at 28°C. mm.	Percentage by weight	Summation percentage	Diameter mm.	Summation percentage	Distribution percentage	Mean diameters plotted
26	.53	0	100	.06	0	0	....
30	.46	0.2	100	.08	5.0	5.0	.07
34	.41	0.3	99.8	.10	12.5	7.5	.09
38	.37	0.3	99.5	.12	24.0	11.5	.11
42	.34	1.1	99.2	.14	36.5	12.5	.13
46	.31	1.6	98.1	.16	49.5	13.0	.15
50	.29	3.0	96.5	.18	62.0	12.5	.17
54	.27	1.7	93.5	.20	73.0	11.0	.19
58	.26	4.4	91.8	.22	81.0	8.0	.21
62	.24	3.0	87.4	.24	87.2	6.2	.23
66	.23	7.2	84.4	.26	91.7	4.5	.25
76	.21	9.7	77.2	.28	95.4	3.7	.27
86	.19	11.6	67.5	.30	97.2	1.8	.29
96	.17	6.4	55.9	.32	98.5	1.3	.31
106	.16	13.1	49.5	.34	99.2	0.7	.33
136	.14	13.0	36.4	.36	99.5	0.3	.35
166	.12	5.6	23.4	.38	99.6	0.1	.37
196	.11	15.3	17.8	.40	99.7	0.1	.39
376	.07	2.5	2.5	.42	99.8	0.1	.41
556	.06	0	0	.44	99.9	0.1	.43

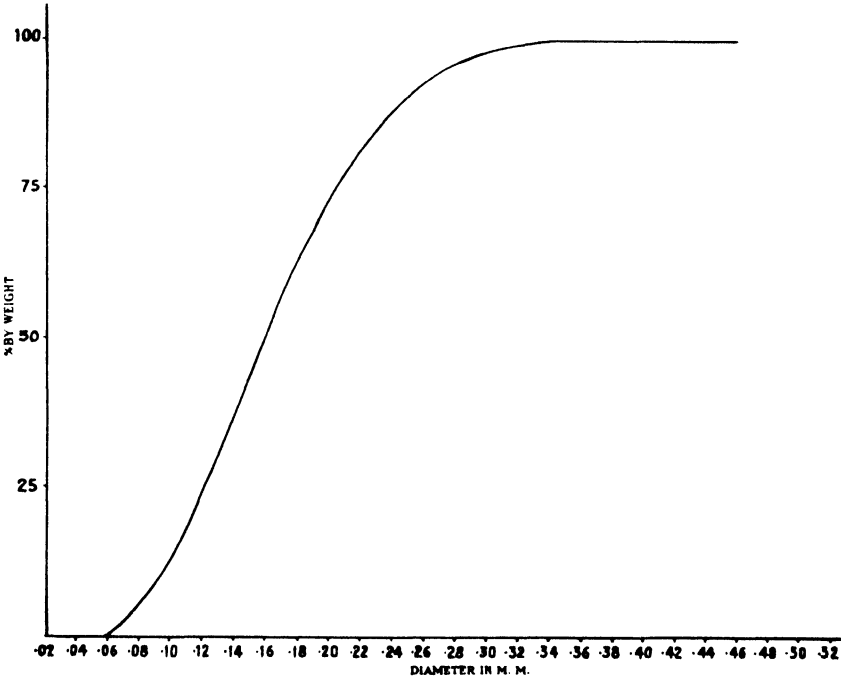



Fig. 7. Summation Curve of Bed Silt (388-S) Sample from the Centre of Jaranwala Distributary

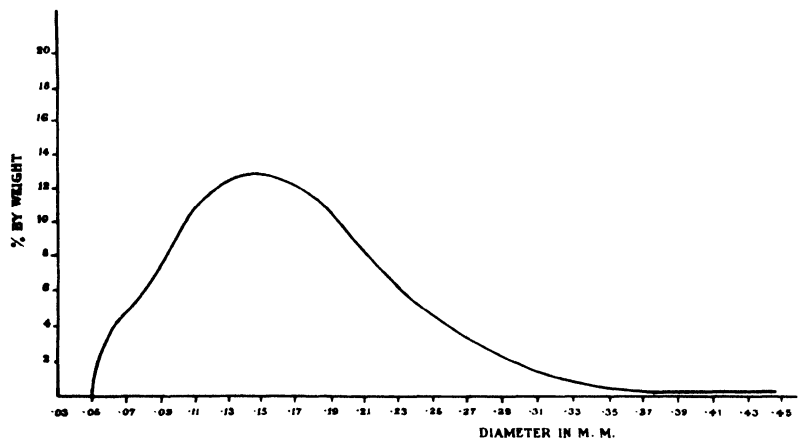



Fig. 8. Distribution Curve of Bed Silt (388-S) Sample from the Centre of Jaranwala Distributary

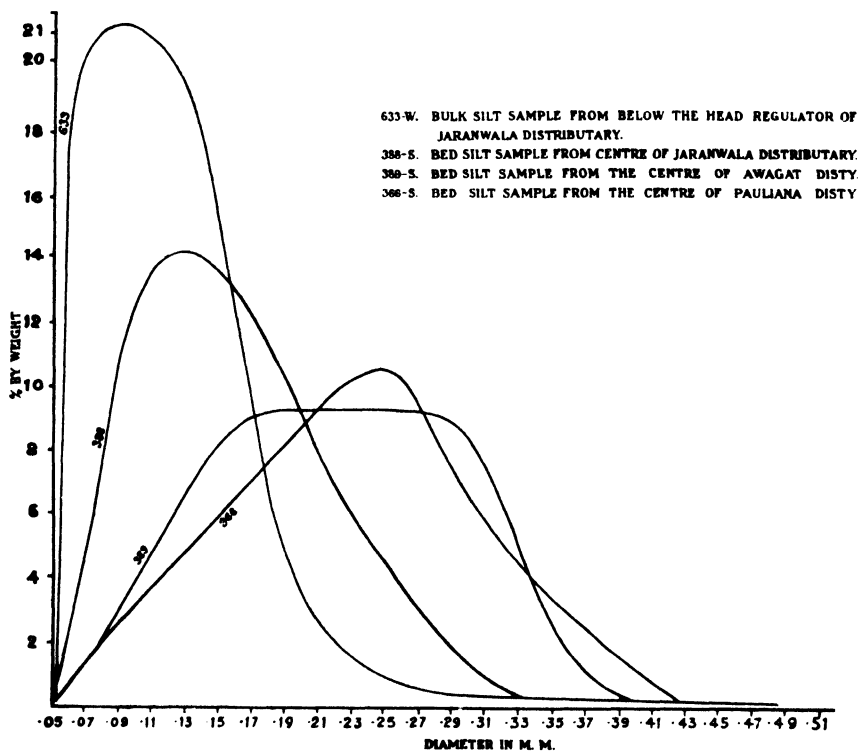



Fig. 9. Distribution Curves

made to express the mechanical composition of soils by "single values" derivable from the summation or distribution curves. There are three such values, each characteristic of the shape of the distribution curve, as follows:

Weighted Mean Size (M). The summation curve of a soil sample gives the percentage of particles below any given size. By taking the reading for two given sizes and subtracting, we can ascertain the percentage of particles whose diameters lie between the two sizes and which may very nearly be assumed to have a diameter lying midway between those two sizes. If this last value is multiplied by the corresponding percentage, and the sum of all such products is divided by the sum of percentages (usually 100), we get a value for the mean diameter of all the particles contained in the sample. This is the weighted mean size, or M, and it furnishes a useful measure of the degree of coarseness of a sample.

Standard Deviation (σ). Not every sample consists of particles distributed in exactly the same way, and it is quite possible that two samples with the same mean size may differ, one having a preponderance of particles with diameters near the mean size, and the other with diameters varying much more widely. Hence it is necessary to know how the various sizes are distributed about the mean size; consequently the standard deviation is calculated as a measure of their dispersion. To obtain this the deviation of each size from the weighted mean size is squared and multiplied by the corresponding percentage and then the sum of such products is divided by the sum of the percentages. The square root of the x quotient gives σ, and the smaller it is the more uniform can the sample be assumed to be.

Schoklitsch Number (K). The maximum diameter of soil particles for an ordinary sample may be taken as 1 mm. In practice, therefore, the summation curve is bounded by the 0- and 1-mm ordinates; and the line RPS may be taken to represent a normal summation curve (Figure 10).

If the area A lying above and to the left of the summation curve is divided by the area B lying below and to the right of the summation curve, the fraction A/B remains constant as long as the limit 0 and 1.0 remains unaltered. This fact was pointed out by Professor Schoklitsch. The constant is referred to as the Schoklitsch number or K, and when not otherwise specified is taken to refer to diameters lying between 0 and 1.0 mm. Should it be desired to specify these limits more particularly, it may be written 0-1.0; in the same way 0-2.0 would refer to mixtures whose summation curves lie between 0 and 2.0 mm.

In dealing with the size distribution of particles in soils we must take note of the fact that the state of aggregation as it is found in nature may be very different from its ultimate structure. The former denotes tilth, and the latter provides a datum line for ex-

pressing the limits of variation in soil texture. It must be remembered that the crumb structure of the soil is merely a single phase in its dynamic history, and therefore it cannot be used for the textural classification of soils, which must be based on their ultimate structure.

"Tilth" is a complicated property of the soil, the determination of which would be extremely useful from the practical standpoint. We can attempt to correlate soil tilth with the dispersion coefficient

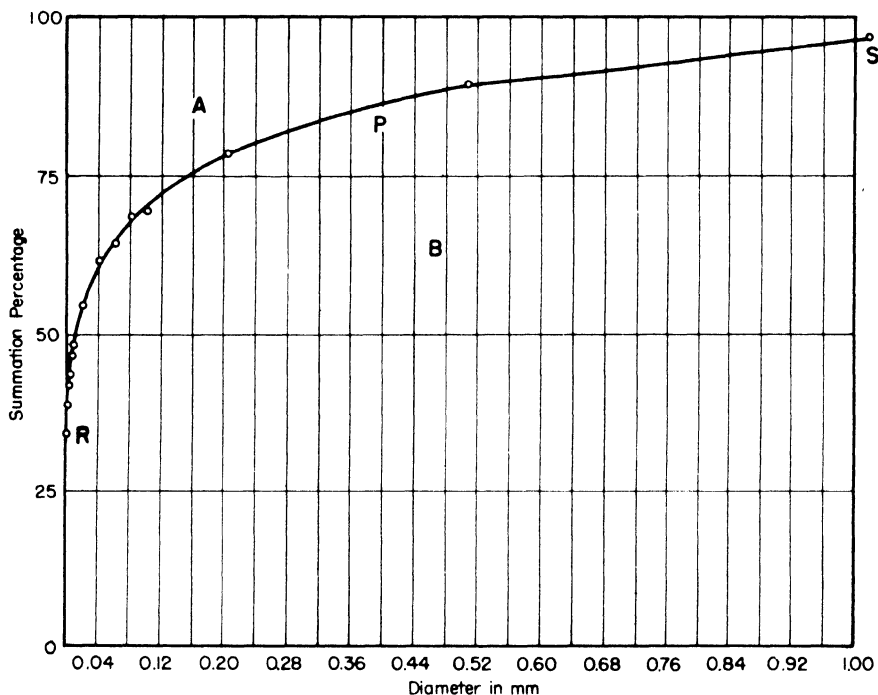



Fig. 10. Example of a Summation Curve

(D.C.), which is measured by determining the percentage of conventional clay (0.002-mm diameter) by the pipette method after leaving the soil in contact with water for 24 hours (referred to as the dispersion factor or D.F.), and expressing it as percentage of the total clay content of the soil obtainable on complete dispersion. In other words

$$\text{D.C.} = \frac{\text{D.F.} \times 100}{\text{clay content}}$$

The dispersion coefficient, therefore, measures the percentage of total clay that can pass into the suspensoid state by simple contact with water, and its value varies from 0 to 100%, depending on whether the soil is completely flocculated or completely dispersed.

The usefulness of the dispersion coefficient for expressing soil

tilth is based on the fact that crumb structure is usually formed by the cementing action of the clay particles, and if these exist in the individual state, all other particles may be present as independent units. In extreme cases, however, it is likely to lead to absurd results. When a small percentage of clay is present in a proportionately large amount of coarser particles, the soil as a whole may be in good tilth even when the dispersion coefficient is 100 per cent. The most logical method of expressing soil tilth would be one based on the entire mechanical analysis of the soil or a function thereof. In other words, tilth, or the state of aggregation of a soil, must give the existing mechanical analysis of the soil as a function of its ultimate analysis. For this purpose, M, K, and σ, which are characteristic constants of any mechanical composition curve, could be used. We may take these values of a soil before and after dispersion, the latter values referring to the ultimate structure. The ratio of these constants may be related to soil tilth. We can then see which of these ratios is the more suitable from the practical standpoint.

Air-dry soils passing a 1-mm mesh were used for this study. The mechanical analysis before dispersion (referred to as the aggregate analysis) and after dispersion (ultimate analysis) was made partly by the pipette method (particles below 0.06 mm) and partly in the Puri siltometer. The siltometer can deal with particles up to 0.6 mm diameter; larger particles were graded by sieving.

Mean diameters, standard deviations, and Schoklitsch numbers were calculated for the two sets of values M_0, σ_0, and K_0, referring to the aggregate analysis and M, σ, and K to the ultimate analysis. These values and their ratios are given in Table 7. A close examination of these constants with reference to the type of soil reveals the following facts.

Alluvial soils give a low value of M (less than 0.05), a low value of σ and a low value of M_0/M. A low value of M associated with low clay content (below 20%) characterizes an alluvial soil. This is exactly what one would expect. Such deposits are well-graded (low σ), and silt gradually merges into clay. Their low clay content and high silt content do not lead to the formation of many aggregates, a fact that is borne out by a low M_0/M ratio.

Black cotton soils (chernozems) have a high clay content, low M value, and high M_0/M ratio. These soils present a high state of aggregation and possess a crumb structure that would be associated with good tilth. Lateritic soils give a high M value and a medium M_0/M ratio. Red ferruginous soils have medium clay, a high M value, a low M_0/M ratio, and a high value for σ. These soils, in fact, behave like a mixture of fine particles abruptly changing into coarse grains. K values run almost parallel to M values and therefore are not likely to prove any better.

In order to illustrate the aggregate and ultimate mechanical analysis curves of two types of soils, the values for an alluvial and a black cotton soil (P.C. 1 and P.C. 2) are plotted in Figure 11. Two typical summation curves that give widely different values of σ are

Summation Percentage.

AFTER DISPERSION P.C.2

AFTER DISPERSION P.C.1.

BEFORE DISPERSION P.C.1

BEFORE DISPERSION P.C.2

Log. Diameter.

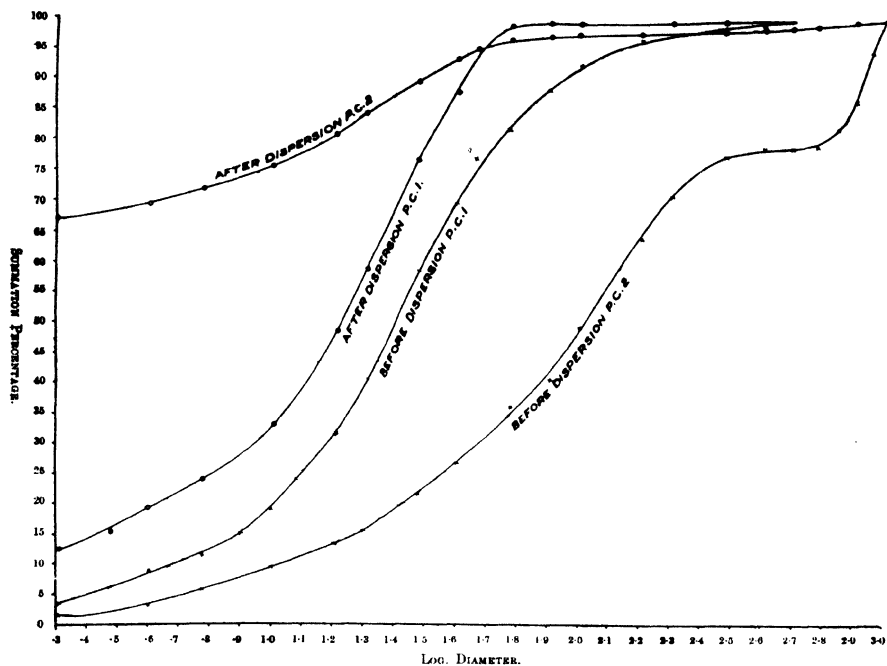



Fig. 11. Summation Curves of an Alluvial (P.C. 1) and Chernozem (P.C. 2) Soil

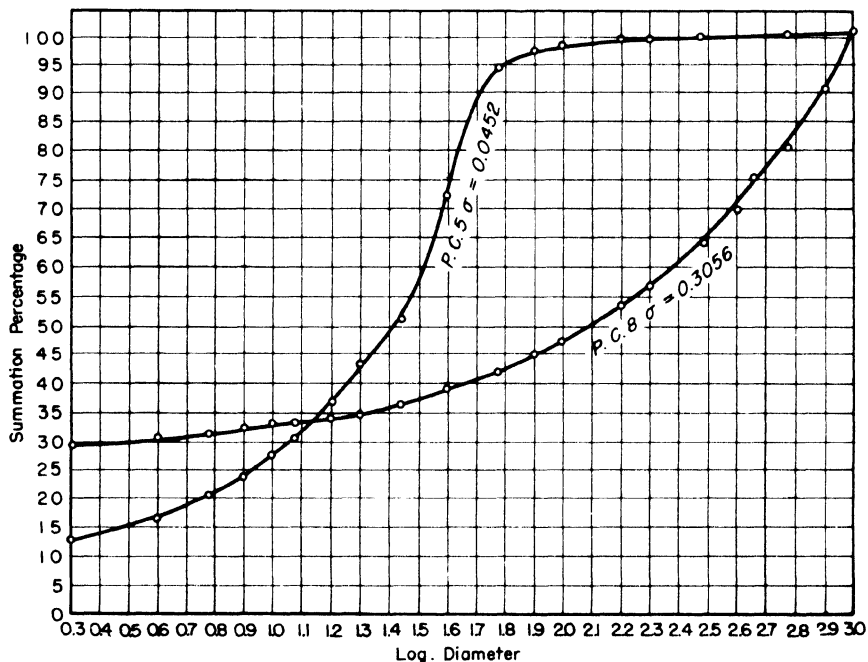



Fig. 12. Summation Curves of Soils to Illustrate a Low and a High Value of Sigma

Table 7. Single value constants relating to the mechanical analyses of soils

Soil Number	Clay per cent (0.002 mm.)		Dispersion coefficient	Mean Diameter		Ratio Mo/M	Standard Deviation		Ratio σ_o/σ	Schoklitsch Number		Ratio Ko/K
	Before dispersion	After dispersion		Before dispersion. Mo	After dispersion. M		Before dispersion. σ_o	After dispersion. σ		Before dispersion. Ko	After dispersion. K	
P.C. 1	3.43	11.48	29.88	0.0452	0.0284	1.59	0.0556	0.0450	1.24	0.0473	0.0292	1.62
P.C. 2	1.50	64.06	2.34	0.2464	0.0361	6.83	0.3044	0.0948	3.21	0.3270	0.0375	8.72
P.C. 3	3.10	68.21	4.54	0.2816	0.0227	12.39	0.3188	0.1020	3.12	0.3920	0.0232	16.89
P.C. 4	4.60	15.56	29.56	0.0581	0.0372	1.56	0.0620	0.0573	1.08	0.0617	0.0380	1.62
P.C. 5	5.73	12.79	44.80	0.0553	0.0376	1.47	0.0550	0.0452	1.21	0.0585	0.0390	1.50
P.C. 6	3.68	29.73	12.38	0.1464	0.0432	3.39	0.1820	0.0840	2.17	0.1720	0.0451	3.81
P.C. 7	21.03	22.80	92.24	0.0512	0.0338	1.51	0.1160	0.0434	2.67	0.0540	0.0350	1.54
P.C. 8	2.00	27.30	7.33	0.2784	0.2784	1.00	0.2712	0.3056	0.89	0.3860	0.3860	1.00
P.C. 9	1.88	22.90	8.21	0.2976	0.2396	1.24	0.2876	q0.2880	1.00	0.4240	0.3151	1.35
P.C. 10	1.08	38.62	2.80	0.2268	0.1400	1.62	0.2568	0.2256	1.12	0.2930	0.1628	1.80
P.C. 11	0.30	35.08	0.86	0.2172	0.1852	1.17	0.2200	0.2516	0.87	0.2870	0.2273	1.26
P.C. 12	1.13	4.18	27.03	0.1380	0.0760	1.82	0.1268	0.0896	1.42	0.1600	0.0823	1.94
P.C. 13	3.05	66.13	4.61	0.3836	0.0380	10.09	0.4332	0.1060	4.09	0.6220	0.0395	15.77
P.C. 14	1.08	26.96	4.01	0.2976	0.0936	3.18	0.2616	0.1640	1.59	0.4240	0.1033	4.11
P.C. 15	1.00	23.51	4.25	0.2632	0.1080	2.44	0.2080	0.1912	1.09	0.3570	0.1212	2.95
P.C. 16	2.98	7.63	39.06	0.1672	0.1164	1.44	0.1144	0.1104	1.04	0.2010	0.1317	1.53
P.C. 17	2.00	14.46	13.84	0.0924	0.0408	2.26	0.1064	0.0488	2.18	0.1020	0.0425	2.40
P.C. 20	0.90	7.29	12.37	0.1520	0.1372	1.11	0.1212	0.1244	0.97	0.1790	0.1590	1.13
P.C. 25	0.80	4.03	19.86	0.1316	0.1340	0.98	0.0784	0.0724	1.08	0.1520	0.1550	0.98
P.C. 26	0.60	30.97	1.97	0.2952	0.2308	1.28	0.2144	0.2248	0.95	0.4190	0.300	1.40
P.C. 33	1.36	3.70	36.76	0.3280	0.3328	0.99	0.2632	0.2580	1.02	0.4880	0.5000	0.98
P.C. 43	2.00	19.71	10.15	0.0506	0.0280	1.81	0.0564	0.0452	1.25	0.0535	0.0290	1.84
P.C. 44	1.20	8.39	14.30	0.0640	0.0488	1.31	0.0580	0.0388	1.49	0.0680	0.0510	1.33
P.C. 45	1.50	10.68	14.04	0.0616	0.0384	1.60	0.0736	0.0520	1.42	0.0656	0.0400	1.64
P.C. 48	2.56	19.79	12.94	0.1192	0.0396	3.01	0.1224	0.0448	2.73	0.1350	0.0410	3.29

given in Figure 12. Note the symmetry of the curve with low σ around the mean diameter as compared to the one with high σ.

It is believed that the textural classification of soils on the basis of M and σ will bring out their characteristic differences much more satisfactorily than the usual practice of giving them descriptive names like sandy, loamy, silty, or clayey.

The ratio of M_0/M not only brings out the state of aggregation or the crumb structure of a soil, but it also shows that the magnitude of this ratio is a characteristic of the soil type. Although the-

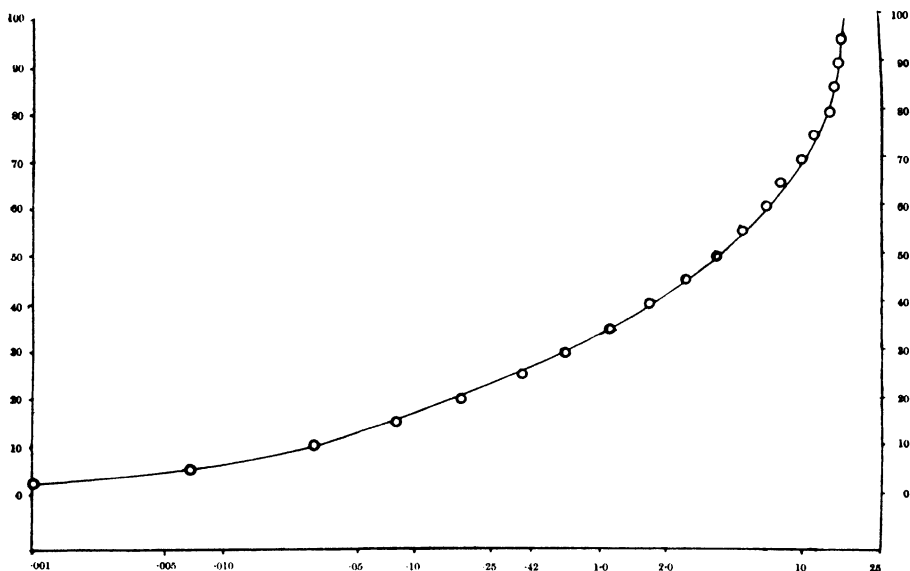



Fig. 13. Summation Curve of a Well Graded Mixture

oretically a soil could be made to have almost any value of M_0/M by suitable treatment in the laboratory, natural soils do acquire a stable structure which, within limits, resists ordinary methods of cultivation. In other words, certain soil types maintain a higher state of aggregation than others. Methods of cultivation of the latter types must be carefully watched, as such soil types are likely to suffer from bad tilth if not handled properly.

A word about the relation between dispersion coefficient (D.C.) and M_0/M ratio. As may be expected, a high D.C. value goes with a low M_0/M ratio, but since the former refers to only one fraction (clay) the relation is merely qualitative.

Soil Grading and Consolidation

The proper grading of mixtures is a first consideration in constructing stable earth roads. The object of grading is to reduce the size of the pores to the minimum. The soil is thus brought to its maximum compactness. The summation curve of a well-graded mixture is given in Figure 13. In an attempt to characterize the

single value constants of summation curves of well-graded mixtures it was discovered that for such curves $M/\sigma = 1$. This fact affords a simple method of deciding whether a certain mixture is well graded. The calculation of M and σ from the mechanical analysis has already been explained.

In an attempt to find a possible correlation between the actual field performance of a dirt road and certain single value constants associated with its mechanical composition, soil samples from a number of earth roads were examined. These roads were a more or less natural consequence of their geographical position rather than of artificial grading. Of course the main difficulty in finding any such correlation was the assignment of some numerical value to road performance. Such terms as "good" or "bad" are not capable of statistical correlations. Certain preliminary observations were made on the basis of visual condition of the road in terms of bad, poor, fair, very fair, good, very good, excellent. These are recorded below:

(1) If the clay content is less than 10% the road will be bad whatever the value of M (mean diameter of the particles).

(2) If the clay content is above 10%, but less than 16%, the road is more likely to be good if the value of M is below 0.1 than above it.

(3) Whenever the clay content is above 16% the value of M, in the majority of cases sampled, is likely to be less than 0.1, and this condition will usually give a good hard road.

Soil Classification Based on Particle Size

It has been made abundantly clear in the foregoing that the only satisfactory method of textural classification of soils is on the basis of their size-distribution curves and single value constants directly calculated from them. However, the arbitrary division of particles into sand (0.02 to 2 mm), silt (0.002 to 0.02 mm), and clay (below 0.002 mm) has the merit of long usage even though it is still uncertain that there is any theoretical justification for such a grouping. It is a handy way of describing a soil, but it is not scientific and is often misleading. The main disturbing factor, of course, is the clay fraction which, as has been explained before, would have none of the properties usually attributed to it if it had no particles smaller than its conventional size (i.e., 0.002-mm diameter). Another disturbing factor is that since the particle size classifications are not universally accepted, the adjectives must be supplemented by numerical values that indicate the particle size range which they describe. This defect may be overcome by adopting the international system of classification into gravel (2 mm), coarse sand (2-0.2 mm), fine sand (0.2-0.02 mm), silt (0.02-0.002 mm), and clay (0.002 mm).

On the basis of its particle size as represented by the preponderance of one or the other fraction, a soil can be designated as silty clay, sandy silt, sandy loam, silty clay loam, etc. This sort of classification, though suitable for certain purposes, can hardly be expected to yield results of any real scientific value.

CHAPTER IX

METHODS OF SOIL DISPERSION PREPARATORY TO MECHANICAL ANALYSIS

Before the introduction of the pipette methods of mechanical analysis, hardly any attention was paid to the preliminary treatment of the soil to insure its complete disintegration into primary particles and their dispersion in water. However, when this aspect of the question was seriously considered, about a dozen methods were suggested for the purpose by different workers. The problem became so acute at one time that the International Society of Soil Science organized a comparison of the various methods on about half a dozen soils of different types, samples of which were sent to a number of laboratories for comparison of methods and report. This cooperative work brought forth a crop of much useful data, but no final conclusion could be drawn. The main difficulty about the whole work was that all the suggested methods were empirical; naturally their comparison left the entire issue undecided.

The dispersion of soil in water is the resultant of two opposing forces. One is the cohesion between the particles, which maintains their state of aggregation and resists any force tending to separate them. The opposing force, on the other hand, is the surface ionization of the particles, which depends on the nature of the saloid comprising the surface. This force is of the same type designated as the electrolytic solution pressure, which causes the molecular disintegration of a solid and sends it into solution. Exactly the same force which, for instance, sends sodium sulphate into solution but keeps barium sulphate as an insoluble precipitate would send a Na-soil into suspension, but keep a Ca-soil as a sediment in water.

With this conception the problem becomes simple, and all the dozen odd methods of dispersing soils for mechanical analysis fall into their natural alignment. We can, therefore, state the method of dispersion in general terms, namely, for complete dispersion the soil must be converted into the sodium saloid which takes place at pH 10.8. We can have a dozen different methods of achieving this end, and the choice will boil down to the ease with which it can be done; but there will be no difference in the ultimate results provided always that the soil has been converted into 100% Na saloid. If by a certain method maximum dispersion is not obtained, we must

carefully examine the various steps of the method used, and invariably it will be found that we have failed to produce 100% Na saloid.

Hitherto, we have taken the estimation of conventional clay (i.e., particles of 0.002-mm diameter) as the ultimate criterion of maximum dispersion. As has been shown in the foregoing, these particles are so coarse, in the physicochemical sense, that if we had no smaller ones the soils would behave like sand as regards their reactivity and moisture absorption. The ultra-mechanical analysis of the clay fraction is, therefore, of the highest importance in judging its total surface, chemical reactivity and moisture absorption at various humidities. In considering the efficiency of dispersion methods, we must push mechanical analysis down to particles of the smallest dimensions possible with the technique at our disposal. Fortunately, by a refinement of the pipette technique we can directly determine particles 0.000094 mm in diameter, and with a hypodermic needle attachment we can go as far as particles of 0.00004-mm diameter.

We can, therefore, examine the efficiency of dispersion methods down to 0.000094 mm or even 0.00004 mm in some cases. The following methods were tried. The list does not exhaust all, but these may be taken as typical of the prevalent or suggested methods of dispersion.

(1) Na_2CO_3-NaOH method: Addition of Na_2CO_3 equivalent to the Ca saloid in the soil, and NaOH equivalent to the free acidoid.

(2) $(NH_4)_2CO_3$ method: Boiling the soil with normal ammonium carbonate solution and continuing the boiling after addition of NaOH or LiOH.

(3) NaCl-NaOH method: Leaching the soil with normal NaCl followed by shaking after the addition of NaOH.

(4) HCl-NaOH method: Leaching with 0.05N HCl followed by shaking after the addition of NaOH.

(5) Alkaline permanganate method: Destruction of organic matter with alkaline permanganate, followed by leaching with oxalic acid and then with dilute H_2SO_4; finally shaking the suspension with the addition of NaOH.

(6) International method A: Destruction of organic matter with H_2O_2, followed by leaching with dilute HCl and finally shaking, with addition of NaOH.

The methods outlined above fall in two catagories: the first three depend on the direct replacement of Ca by Na saloid without the removal of $CaCO_3$ in the soil. The last three aim at the removal of cationic Ca as well as $CaCO_3$, thus converting the soil into an acidoid which is subsequently neutralized with NaOH. It is clear that all the treatments ultimately aim at the production of Na soil, and the final addition of NaOH to pH 10.8 completes the neutralization of the acidoid. Six soils were used for this comparison. These were selected from a larger collection to include as many diverse char-

acteristics as possible. Some of the more important single value constants for these soils are given in Table 8.

Results of ultra-mechanical analyses are recorded in Table 9. Complete data are given in the case of P.C. 13 soil; for the rest only the coarsest and finest fractions are recorded.

Table 8. Single value constants of soils used for dispersion

Soil P.C. No.	pH	$CaCO_3$ per cent	Ca saloid m.e./100 gm.	Na + K saloids m.e./100 gm.	Mg saloid m.e./100 gm.
13	8.53	1.50	55.6	....	....
116	4.70	0	3.8	0	0.4
118	4.75	0	4.4	2.5	1.0
123	8.92	3.35	12.0	17.4	2.8
142	7.80	0.725	40.4	1.8	0.9
166	5.11	0	13.2	0	2.5

Table 9. Comparison of different preliminary treatments for the ultra-mechanical analysis of soils

Soil No.	Limiting diameter mm.	Percentage of particles with different treatments					
		Na_2CO_3-NaOH	$(NH_4)_2CO_3$-NaOH	NaCl-NaOH	HCl-NaOH	$KMnO_4$-NaOH	H_2O_2-NaOH
13	.002	60.1	55.6	60.5	58.8	57.2	60.7
	.001	59.9	53.2	57.9	56.9	55.4	58.3
	.00043	43.5	36.0	47.8	48.6	49.2	47.6
	.00023	27.6	18.5	41.1	46.2	46.6	43.6
	.00016	16.2	10.0	31.7	45.0	45.3	43.6
	.000094	16.3	11.5	33.0	45.7	45.1	42.2
116	.002	22.5	24.1	21.9	24.3	23.4	24.8
	.000094	11.6	8.5	9.1	15.5	13.8	14.6
118	.002	28.3	28.1	27.3	28.4	28.0	27.7
	.000094	10.4	11.2	11.0	15.7	14.6	13.5
123	.002	88.2	86.2	87.4	90.9	78.5	83.4
	.000094	25.5	20.3	32.4	39.2	31.1	29.5
142	.002	60.4	56.0	60.4	57.8	58.7	60.4
	.000094	17.0	16.7	39.6	42.1	45.8	43.8
166	.002	56.8	57.1	59.7	56.2	62.7	58.5
	.000094	19.8	15.8	27.8	31.5	44.6	29.1

It is clear from these results that all methods of treatment give practically the same results as regards conventional clay. Methods involving acid treatment, however, give a higher percentage of finer fractions than the others.

The failure of the methods involving no acid treatment in dispersing fractions finer than clay may be due to two causes: (a) The presence of $CaCO_3$ left over in the soil might furnish enough Ca ions to exercise a flocculating action on some of the finer fractions. (b) Conversion of the Ca saloid into Na saloid is not complete in these methods, and since this element is largely responsible for the cementing action between the various particles, some of the finer aggregates are not broken up into ultimate units.

The first possibility can be easily tested by conducting an ultra-mechanical analysis of a completely dispersed Na soil with and without the addition of $CaCO_3$. The results of such a test with all the soils listed showed that in no case was there any decrease in the amount of ultra-clay on the addition of $CaCO_3$. The second assumption can be tested by determining residual Ca saloid in the soils after the preliminary treatments in every case. This was done in the various soils after subjecting them to the different treatments, exactly as in the case of mechanical analysis. The residual Ca saloid was determined by the K-oxalate-acetate-carbonate method. The results, given in Table 10, show that the failure of some of the methods to bring about maximum dispersion of ultra-clay is most probably due to the incomplete conversion of the Ca

Table 10. Residual Ca saloid in soils after different dispersion treatments

Soil No.	Residual Ca saloid. Milliequivalents per 100 gm. soil					
P.C.	Na_2CO_3	$(NH_4)_2CO_3$	NaCl	HCl	$KMnO_4$	International
13	5.4	5.8	3.2	0	1.6	1.4
116	0.8	1.0	0.6	0.4	0.8	0.8
118	0.8	1.4	1.0	0.8	0	0.8
123	6.2	5.8	5.6	1.2	1.6	1.4
142	4.6	4.6	1.0	0.6	0	1.6
166	1.4	1.6	1.0	0	0.8	1.0

into Na saloid. It appears that 0.05N HCl treatment is the most effective method for removing all the cations and gives the maximum amount of Na saloid on subsequent treatment with NaOH.

Since for maximum dispersion of the soil acid treatment appears to be necessary, it is important to know whether such treatment might result in the dissolution of some of the finest particles. In order to find out how far this objection is valid, three typical soils were subjected to the following treatments:

(1) Simple leaching with 0.05N HCl until filtrate is free from Ca ions.

(2) Same as (1) followed by further leaching with 500 cc of 0.05N HCl.

(3) Same as (1) followed by further leaching with 1000 cc of 0.05N HCl.

(4) Same as (1) followed by further leaching with 500 cc of 0.2N HCl.

(5) Same as (1) followed by further leaching with 1000 cc of 0.2N HCl.

(6) Same as (1) followed by further leaching with 500 cc of N HCl.

(7) Same as (1) followed by further leaching with 1000 cc of N HCl

It will be seen that acid treatment, both in the volume of solution as well as its strength, has been pushed much beyond the usual amount recommended for the purpose. Complete ultra-mechanical analysis was done on the soils after the various treatments after

neutralizing them with NaOH to pH 10.8. Results for only two fractions, namely conventional clay and the finest ultra-clay (particles of 0.00004 mm diameter), are recorded in Table 11.

It will be seen that prolonged leaching with acid of much higher strength than that generally recommended for the purpose has produced no change in the results of ultra-mechanical analysis. The soil colloids in fact, as far as can be judged from the behavior of these three typical soils, are quite stable and resist the action of dilute HCl leaching. Leaching with normal HCl appears to have some slight effect in reducing the content of the finest particles of ultra-clay, but this is an extreme case and acid of this strength is never recommended in any preliminary treatment for dispersion.

Table 11. Effect of preliminary acid treatment on clay (.002 mm.), and ultra clay

Treatment	Percentage of clay and ultra-clay in various soils.					
	P.C. 6		P.C. 13		P.C. 123	
	Clay	Ultra-clay	Clay	Ultra-clay	Clay	Ultra-clay
1	33.8	14.5	60.1	27.2	85.5	12.9
2	34.2	14.2	60.5	28.1	84.6	11.5
3	34.8	14.6	61.5	27.8	83.8	12.6
4	34.4	13.8	59.8	27.1	86.2	13.0
5	33.7	14.4	58.7	26.6	86.0	12.0
6	33.5	12.6	56.9	25.2	80.1	10.3
7	32.4	12.6	57.4	25.5	78.2	10.1

Humus is supposed to play an important part in the dispersion of soils by acting as a cementing material and thereby preventing the dispersion of soil aggregates. This is the basis of the international method of preliminary treatment in which humus in the soil is destroyed by oxidation with H_2O_2. A more effective method of removing humus is by oxidation with alkaline permanganate. We have already seen that as far as conventional clay and ultra-clay are concerned, the results with and without the permanganate treatment are practically the same. The subject, however, required a more thorough examination of a larger number of samples. Results with 15 soils are recorded in Table 12; only the conventional clay and ultra-clay (0.00004 mm diameter) are given, since the intermediate sizes led to the same conclusion. A careful examination of the data in Table 12 reveals the following facts:

(1) When soils are not freed from humus, consistently higher values are obtained for all the fractions.

(2) The difference in the two sets of values obtained for a soil is of the order of the percentage of humus present in that soil. It is interesting to note in this connection that humus itself in alkaline solutions has no ultra-mechanical analysis and all particles appear more or less to be of uniform diameter up to the limit to which

ultra-mechanical analysis can be pushed. In fact, Na humate is in truly colloidal solution which shows no sign of settling within any measurable time limit.

(3) Humus, on account of its solubility in NaOH, no longer acts as a cementing material if dispersion is brought about by the HCl-NaOH method. In this case humus is counted as clay or ultra-clay.

(4) If the mechanical analysis of the mineral colloids only is desired, the preliminary destruction of organic matter in case of soils rich in humus is essential. Generally for average soils it is not necessary. Alternately, humus can be determined separately and its percentage subtracted from the weight of the various fractions.

Table 12. Clay (.001 mm.) and ultra-clay (.00004 mm.) in soils with and without treatment with alkaline permanganate

Soil No.	Humus per cent	Clay		Ultra-clay	
		(a)	(b)	(a)	(b)
116	1.2	24.8	23.3	6.0	5.6
183	0.5	8.4	10.2	0.8	1.2
242	0.8	15.8	15.2	4.5	3.2
243	0.5	11.1	9.5	2.0	2.0
244	0.2	37.0	36.5	5.2	7.6
245	0.5	30.1	34.8	9.8	7.8
250	0.45	8.2	10.4	3.6	2.8
M-8	4.5	30.0	27.1	10.8	8.1
M-12	4.1	24.0	19.2	9.5	6.0
M-19	6.3	33.2	27.5	11.2	7.0
M-40	5.25	58.2	52.4	21.5	16.6
M-41	3.77	63.4	59.0	9.8	6.8
P.C. 2	5.78	20.6	15.2	9.2	5.0
P.C. 3	4.66	23.4	20.5	10.1	7.2
P.C. 5	7.28	23.1	16.8	11.2	6.6

(a) Untreated
(b) Humus destroyed by alkaline permanganate.

(5) The alkaline permanganate method of destroying organic matter does not affect the mineral colloids and therefore cannot be considered as too drastic a preliminary treatment of the soil for mechanical analysis.

The effect of heating a soil to various temperatures is very interesting. Heating to 100%C produces no difference in its mechanical or ultra-mechanical analysis; but heating above this temperature has a pronounced effect. First the finest particles start to cement together and with further rise of temperature coarser and coarser particles begin to aggregate. Typical results with two H soils are given in Table 13.

A close examination of these shows the extraordinary stability of soil particles and demonstrates that particle size distribution is the most important distinguishing feature of soils. The results also

throw light on the geometrical configuration of the particles as they exist in soils. It has been generally assumed that soil particles are coated with a colloidal layer which has a gel-like structure. The nature of this colloidal layer has been conceived vaguely, for it is not understood how this layer adheres to the particles and why it does not come off. The main difficulty has been the failure to recognize the existence of particles smaller than the conventional clay, where all mechanical analysis stops.

Table 13. Effect of heating the soil on its mechanical and ultra-mechanical analysis. Soils P.C. 13, and P.C. 123.

Size of particles mm.	Soil No. P.C.	Percentage of particles when heated at various temperatures									
		No heating	100°C	200°C	300°C	400°C	500°C	600°C	700°C	800°C	900°C
.06	13	90.8	89.5	91.4	90.8	61.8	45.6	45.5	41.0	41.0	40.5
	123	98.8	99.2	99.0	99.0	97.0	72.8	61.2	52.4	48.1	45.6
.02	13	82.8	82.9	82.5	82.7	41.4	26.2	22.6	21.2	22.2	18.8
	123	93.2	91.2	91.2	92.5	92.6	52.8	36.2	29.0	25.2	22.4
.01	13	70.6	72.2	73.5	72.8	30.2	19.1	16.4	15.4	14.7	11.9
	123	90.2	89.1	89.6	90.8	90.4	45.2	29.1	20.4	17.1	14.8
.005	13	63.6	65.0	66.2	65.2	24.5	14.1	12.2	10.6	10.5	8.2
	123	89.3	86.4	87.8	90.0	86.8	39.2	23.8	16.2	14.0	11.0
.002	13	60.3	59.2	61.2	57.5	19.5	11.2	8.5	6.0	6.5	6.4
	123	85.5	86.9	86.6	85.9	80.9	20.5	17.8	9.5	7.8	4.8
.001	13	57.7	56.7	57.2	54.4	18.2	8.4	6.8	5.4	5.8	4.2
	123	81.5	81.8	81.8	77.4	68.9	26.6	16.0	9.2	5.9	4.1
.00063	13	52.9	54.4	54.2	49.6	16.4	7.6	5.4	5.0	5.2	3.2
	123	74.2	73.6	75.0	70.0	54.5	21.6	12.6	5.8	3.8	3.6
.00025	13	49.2	49.1	41.7	36.5	14.7	6.3	5.5	4.2	2.8	1.2
	123	52.2	50.8	52.3	47.0	28.2	13.6	9.4	5.1	3.6	3.0
.0001	13	41.0	43.2	27.2	17.3	13.5	4.8	3.4	2.8	2.4	0.9
	123	25.8	25.5	22.0	20.5	16.8	10.5	6.6	4.1	3.5	2.6
.000063	13	35.7	37.9	22.1	16.0	11.0	4.5	2.9	2.2	1.9	0
	123	18.6	18.2	16.2	14.2	11.2	9.0	5.1	3.9	3.2	2.2
.00004	13	27.2	28.2	19.2	11.2	10.5	3.9	2.5	1.7	1.0	0
	123	12.4	12.8	11.9	10.5	7.5	7.0	4.6	3.2	2.6	1.8

To overcome the fact that these particles are really too coarse in the colloid chemical sense, it has been assumed that, though coarse themselves, they have large surface areas due to the gel coating. Ultra-mechanical analysis has rendered this assumption unnecessary. We know now that conventional clay is only the upper limit of the finest particles, which extend almost to molecular dimensions. In soils we have colloid chemistry in the making: a state of continuity which emphasizes that there are no abrupt breaks in the scheme of natural forces. Here mono-molecules merge into poly-molecules, and poly-molecules into aggregates of increasing coarseness; each aggregate has its position in the size distribution and makes its distinct contribution toward the chemical reactivity of the entire soil. There is no such thing as one particle forming a coating on another, except in a very crude sense when we talk of the crumb structure. Every particle has its individual identity, which is maintained until break-down occurs by natural forces of weathering, which cover a period of several centuries. When a soil is heated, the finest particles are the first to be affected. The content of this fraction decreases appreciably, but does

not disappear altogether, which shows that the limit of ultra-clay is purely a reflection of the inadequacy of scientific equipment to resolve it any further. Actually it must contain finer and still finer particles, which are the first to fuse together to form larger particles.

In dealing with the structural characteristics of soils a distinction must be made between molecular aggregates and particle aggregates. The former is a compact structure with no interstices, whereas the latter is a loose association of particles with considerable gaps between them. Every particle in the ultimate mechanical analysis of a soil represents a molecular aggregate like any other solid matter in mass. On drying, the various particles form aggregates which are water-stable unless the soil is a Na saloid of pH value 10.8. We must distinguish between ultimate mechanical analysis, when primary particles are dispersed as independent units, and aggregate mechanical analysis in which compound particles are taken as units.

CHAPTER X

DISPERSION OF SOILS BY MECHANICAL METHODS

We have seen that the only method of attaining maximum dispersion is the conversion of the soil into a Na saloid of pH 10.8. Though some soils show maximum dispersion even at a lower pH value, all soils show it at pH 10.8. We have also seen that this conversion can be brought about most effectively when the soil is first converted into an acidoid and then neutralized with NaOH to pH 10.8. The advisability of using chemicals for soil dispersion has always been the subject of heated discussion, and opinion is still divided on this question. Several workers have passed judgment in favor of one or the other method. The main difficulty has been the lack of an absolute standard of reference, for no one has ever been quite sure that the maximum dispersion, as measured by the clay content, does really represent the ultimate breakdown of all compound particles into their primary units. With the fundamental basis of discrepancy cleared up by the recognition of the importance of pH value, we have at our disposal an absolute standard for comparison. We are at least reasonably sure that the maximum clay, as obtained by the HCl-NaOH method, is not exceeded by any other known method. We can therefore examine purely mechanical methods of dispersion to see how far they fall short of the maximum clay as obtained by chemical methods, which are all equally effective as regards conventional clay.

Among the mechanical methods of dispersion one of the oldest is boiling, which is probably still used in certain laboratories. Comparatively recently (1926) endeavors have been made to obtain the effect of "cold boiling" by drawing air through the suspension and obviate the objectionable features of heating. Simple rubbing in water with a stiff brush or rubber pestle was another early procedure used by Beam (1911). Whittles (1924) used a vibrating machine to disperse soil samples, and Olmstead (1931) used supersonic waves for the purpose. The supersonic vibrations were produced by a piezo-electric quartz crystal immersed in an oil bath. The energy was transmitted through the oil into an Erlenmeyer flask containing a water suspension of the soil. The arrangement, however, is far too costly to justify its use for routine purposes, especially as the results are practically the same as those obtained by rubbing with

a rubber pestle. Bouyoucos (1927) used an electric drink mixer to disperse his samples. This procedure was slightly modified by Baver (1928).

It must be remembered that the dispersion of soil particles is largely a question of overcoming the cohesion between the particles. Physico-chemically it is brought about by neutralizing the acidoid with NaOH to pH 10.8. Physically the choice must fall on one or more of the half dozen methods referred to in the foregoing chapters. It might be mentioned, however, that no purely mechanical method can bring about the disintegration or dispersion of ultra-clay particles, as they are too small for any mechanical disruptive force to reach them. But for most purposes the estimation of conventional clay is all that is necessary, and the break-down of particles to the extent of this lower limit is possible by purely mechanical means of dispersion without the addition of any chemical.

The choice of a H soil for a comparison of the various methods is preferable because it is the starting point for the gradual introduction of bases. Not only is it the most important basic material for all soil studies, but its use is particularly appropriate in this case, as the internal cohesion is probably maximum. If a mechanical treatment is successful in this case, the efficiency of the method for all types of soils will be assumed. Besides, a H soil is often required at maximum dispersion for several physico-chemical measurements. This object can be accomplished by converting it first into a Na soil without allowing it to dry. For maximum dispersion down to ultra-clay particles of the smallest dimensions this is the only way, but if the lower limit of dispersion is the conventional clay, then purely mechanical methods are applicable.

For comparing the various mechanical methods of dispersion treatments which require elaborate mechanical contrivances were left out of consideration, for it was felt that unless a physical method could be made at least as simple as the admittedly efficient chemical treatments, it would not find favor generally from the practical point of view. A black cotton soil was used in the first instance; it was converted into a H soil by the usual 0.05N HCl treatment, and air-dried. The maximum clay percentage in the soil was 55. The following methods of dispersion were tried.

(1) Boiling, both "cold" and hot and with sand.

(2) Rubbing with a rubber pestle.

(3) Simple shaking in a mechanical shaker with and without rubber balls or sand.

To summarize the results: boiling from 30 minutes to 4 hours with 200 to 400 cc of water for 10 grams of soil gave values for clay (0.002 mm) ranging from 18 to 37%. The latter value was obtained when boiling was continued for 4 hours. The addition of sand to the boiling suspension had no appreciable effect. "Cold boiling" was the least effective of all, giving a value of 3.5% clay on 30 minutes' cold boiling against 21.5% for hot boiling for the same time.

Rubbing the soil for 30 minutes in an agate mortar with a rubber pestle by hand with 10 cc of water for 10 grams of soil gave 24.6% clay, as against 55.6% when rubbing was done with a mechanically rotated rubber pestle. When the amount of water was increased from 10 to 30 cc, the clay dispersed fell from 55.6 to 42.8%. When the amount of water was increased from a 1:1 ratio, the soil particles had a tendency to float and thus escape the grinding action of the pestle.

A mechanical shaker is the simplest and most widely used contrivance for dispersing soils. Its effectiveness can be enhanced by the addition of rubber balls or sand to the suspension. Shaking the suspension with coarse sand (1.5 mm diameter approximately) gave the highest yield of clay. Shaking is continued for 24 hours using a soil : sand ratio of 1:5. Neither the temperature, nor the volume of

Table 14. Comparison of clay contents obtained by dispersing natural as well as H-soils by the proposed sand method and the chemical method

Difference between clay per cent by the two methods	number of soils showing difference of this order	
	Natural Soils	H-soils
0 to 1.0	51	6
1.1 to 2.0	27	7
2.1 to 3.0	29	5
3.1 to 4.0	22	2
4.1 to 5.0	17	5
5.1 to 6.0	1	5
6.1 to 7.0	3	6
7.1 to 8.0	0	3
8.1 to 9.0	0	5
9.1 to 10.0	0	5
10.1 to 15.0	3	8
15.1 to 20.0	3	0
20.1 to 25.0	1	2

water used (which can be varied from 25 to 300 cc), has any effect on the rate of dispersion or the maximum dispersion obtained.

Results with a drink mixer or simple shaking are of a lower order. The sand method requires practically no attention during the time the suspension is being shaken, and beyond adding the requisite amount of sand there is no preliminary treatment involved. The sand used is easily recovered after dispersion by passing the suspension through a seive of 1-mm mesh, and can be used repeatedly.

In view of the importance of these results in choosing for practical use a purely mechanical method of dispersion, and since chemical methods are almost universally used in soil laboratories, it became imperative that the sand method be compared with the chemical methods of dispersion. For this purpose 157 soils were used. These soils had been collected from different parts of India and represented practically all types. Also 59 H soils were compared by the two methods. The results in Table 14, for convenience of

space, are tabulated as difference between the two methods against the number of soils showing differences of that order.

For H soils the chemical method used was the addition of sufficient NaOH to bring the pH of the suspension to 10.8. For natural soils the Na_2CO_3-NaOH method of dispersion was employed, in which Na_2CO_3 equivalent to the Ca saloid in the soil is added, together with sufficient NaOH to raise the pH value to 10.8. The latter method may be regarded as the least drastic of all the chemical methods, and therefore most appropriate for comparison with a purely mechanical method. From a critical examination of the data the following conclusions were drawn:

(1) The majority of natural soils (15) gave maximum dispersion with the sand method and the results agreed with the Na_2CO_3 method.

(2) Some natural soils (7 out of 157) gave higher values with the sand method than with the Na_2CO_3 method. All these seven soils, though from vastly different localities, belonged to one type, namely, shale. The low values for these soils in the chemical method were due to the failure of the Na_2CO_3 method to bring about complete dispersion. When these soils were acid-treated and then shaken with NaOH at pH 10.8, they dispersed completely and the values agreed with the sand method.

(3) Only one natural soil gave a higher value by 7.6% with the Na_2CO_3 method.

(4) Six natural soils showed flocculation when the volume was made up after shaking with sand. When the soil had settled and the clear supernatant liquid was poured off and replaced by fresh distilled water, the suspension was stabilized. The flocculation in these soils was due to salts, and when these were removed by a preliminary leaching with water, the dispersion was complete with sand.

(5) Two natural soils presisted in flocculating after dispersion with sand. No amount of preliminary leaching with water improved matters, though a small amount of alkali stabilized the suspension and the yield of clay was maximum. These soils had low pH values and contained only Ca saloid. On converting the latter into acidoid by HCl treatment, the soil could be dispersed completely by the sand method. The dispersion was even slightly enhanced by the addition of $Ca(OH)_2$, but when the amount of $Ca(OH)_2$ was increased to the quantity originally present, flocculation took place.

(6) The agreement between the chemical and mechanical methods is not so close in the case of H soils. This is evidently because such soils have very unfavorable pH values for dispersion, as they are not only the least ionized, but contain some of the sesquioxides, which have a flocculating effect.

The results, on the whole, leave no doubt that the sand method is an effective means of dispersing natural soils. A number of natural soils were subjected to complete mechanical analysis and the sum-

mation curves obtained by the two methods were found to be identical. There is thus no breakdown of the coarser fractions into particles that did not originally exist in the soil. The remarkable agreement between the mechanical and chemical methods of dispersion shows that neither one nor the other is too drastic and that both give the size distribution of particles as they exist in soils.

The efficiency of the sand method for dispersing soils led to the speculation that this treatment may be too drastic for some soils, and in addition to breaking up the aggregates may cause some of the coarse primary particles to disintegrate as well. A few soils, therefore, were shaken with sand for seven days instead of the prescribed 24 hours' shaking. The percentages of various fractions obtained on seven days' shaking were the same as those obtained on 24 hours' shaking, indicating that the sand method is not so drastic as to break up primary particles.

The sand method, as pointed out before, presents the possibility of obtaining normally undispersed H soil in a dispersed condition. The soil thus dispersed no longer remains so if it is dried. There is no known method by which a dispersed H soil can be preserved in the dry state so that on coming into contact with water it gives a suspension at maximum dispersion. The fact that softer crumbs are produced when a soil wetted with alcohol is dried indicated the possibility of dispersing it in alcohol in the first place. Filtration of an alcohol-dispersed soil is rapid, and on drying it falls to powder. It was found that although the soil could be dispersed, as in the case of water, by shaking with alcohol in the presence of coarse sand and there was no difficulty in filtration, it could not be redispersed in water on drying. This was at first attributed to the presence of traces of water in the alcohol. The soil was, therefore, dispersed in alcohol with sand, filtered and washed with absolute alcohol, then with benzene and finally with ether. It was then dried in a current of air and kept in a desiccator until redispersed in water. Even with this treatment the soil could not be redispersed fully, though dispersion was much greater than when water-saturated dispersed soil was dried.

This leads to another interesting aspect of the question. Does the particle aggregation follow some fixed geometrical pattern, or does it take place haphazardly? Just as we have mechanical analysis representing the primary particles, we can have aggregate analysis which refers to the size distribution of water-stable aggregates. It is important to know if this aggregate analysis has a fixed pattern for a particular soil. Again, when a completely dispersed soil flocculates and particles form aggregates, do they do so haphazardly or is some order to be observed in the formation of such aggregates? In what follows an attempt will be made to throw light on these questions.

Three typical soils were selected for this purpose. These represented different types: P.C. 6, a laterite; P.C. 13, a black cotton

soil; and F.R. soil, a typical Punjab alluvium. These soils were repeatedly dispersed and dried and the dried samples mechanically analyzed by means of the Chaino-hydrometer and the Puri siltometer previously described. The method employed for dispersion consisted in shaking the soil suspension for 24 hours in a mechanical

Table 15. Reproducibility of results of aggregate mechanical analysis on repeated dispersion and drying of soils

Soil No.	Replicate	Summation percentages of various limiting diameters mm.									
		.002	.005	.01	.02	.06	0.1	0.2	0.3	0.4	0.5
6	a	6.0	6.8	10.8	25.3	58.2	67.5	84.0	95.0	99.0	100
	b	5.2	8.5	11.5	24.2	56.5	62.5	80.2	93.5	97.5	100
	c	5.6	8.1	10.8	24.2	55.5	64.8	81.5	95.0	97.8	100
F.R.	a	11.9	18.4	30.4	44.4	77.8	93.5	98.0	99.0	99.9	100
	b	10.8	18.0	30.1	43.8	75.5	92.5	97.5	99.0	99.6	100
	c	10.8	17.1	29.5	43.8	76.2	92.2	94.5	98.2	99.0	100
13	a	1.4	5.3	9.7	19.1	29.4	39.3	61.0	75.2	82.1	93.2
	b	1.6	7.1	10.4	21.1	29.9	38.8	61.7	72.2	84.4	94.9
	c	1.2	6.6	10.0	21.4	30.8	38.8	58.8	70.2	83.4	93.5

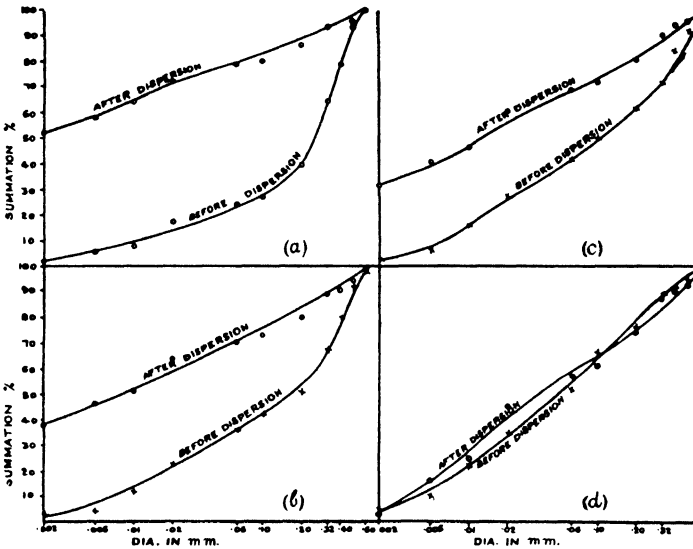



Fig. 14. Effect of Removal of Increasing Amounts of Clay on State of Aggregation of Soil P.C. 13

(a) Sample dispersed and dried without removal of clay
(b) 50 per cent of total clay content removed
(c) 60 per cent of total clay content removed
(d) 90 per cent of total clay content removed

shaker with coarse sand, as in this method the soil is dispersed without converting it into Na saloid. The result is that the dispersed soil on drying, unlike a Na soil, will not redisperse in water, and its aggregate mechanical analysis reveals the state of aggregation exactly as it exists in the dry soil.

The results given in Table 15 show that a dispersed soil when dried does acquire a stable and reproducible state of aggregation. These results are very important and give added weight to the aggregate mechanical analysis of soils. They confirm the conclusion already arrived at from a study of the dispersion coefficient of soils, namely, that natural soils have a crumb structure which is characteristic of their ultimate mechanical analysis and therefore is not likely to change from day to day. Whereas [illegible] mechanical analysis would give a measure of its chem[illegible]vity and other fundamental physicochemical properti[illegible]egate mechanical analysis would reveal to a large ext[illegible]ior in the field, such as cohesion, permeability, aeratic[illegible]Reference may again be made to the ratio M_0/M, i.e., the ratio between the mean diameters of particles with and without dispersion. Since clay is the cause of aggregation, its gradual removal is bound to narrow the difference between aggregate and ultimate mechanical analysis of a soil. This is brought out in a striking manner in Figure 14, in which are plotted the summation curves of soil P.C. 13, with gradual removal of clay by repeated sedimentation and pourings. It will be seen that when 90% of the total clay is removed, the aggregate and ultimate mechanical analysis summation curves coincide.

Similarly gradual addition of clay results in a widening of the difference between the aggregate and ultimate mechanical analysis.

CHAPTER XI

FLOC VOLUME

Another aspect of the state of aggregation is the formation of aggregates on flocculation of a suspension. It is of interest to know whether these aggregates bear some relation to the crumb structure of the soil on drying or to its ultimate mechanical composition. For this purpose a completely dispersed H soil suspension was flocculated by the addition of 10 cc of normal $CaCl_2$ to 2 grams of soil in 100 cc of water. The flocculated suspension was kept for ten days to produce water-stable flocs and then was analyzed in the Puri siltometer. The results of this analysis for soil P.C.13 are given in Figures 15 and 16 in the form of distribution curves.

It is clear that the curves are reproducible; in other words, the state of aggregation is not due to chance coalescence of the particles, but takes place in accordance with some definite relationship to the mechanical composition of the soil. It is interesting to note that for soil P.C.13 neither the shape of the distribution curve nor the mean diameter (M) varies very much when different flocculants are used, though NaCl appears to give a somewhat lower value for the mean diameter. This is not surprising in view of the peculiar behavior of Na soils. Potassium, on the other hand, behaves like a divalent ion.

It was felt that the concentration of NaCl used for these experiments might not have been sufficient to bring about the same state of aggregation. Raising the concentration of the solution from 0.1 to 0.2 normal, however, did not materially affect the distribution curve. These results show, therefore, that apart from their dispersibility Na soils give finer crumbs. It is for this reason that a dried pellet of Na soil has the highest cohesion of all cations.

These observations raise another interesting point. If the aggregate analysis of a flocculated soil is characteristic of its ultimate mechanical analysis, then the floc volume must also bear some relation to it. Clay is the fraction which contributes by far the most toward a bloated floc volume, which but for its presence, would shrink to the normal size of any sediment. It is interesting to know what size of ultra-clay is mainly responsible for it and whether there is any relation between ultra-clay and floc volume.

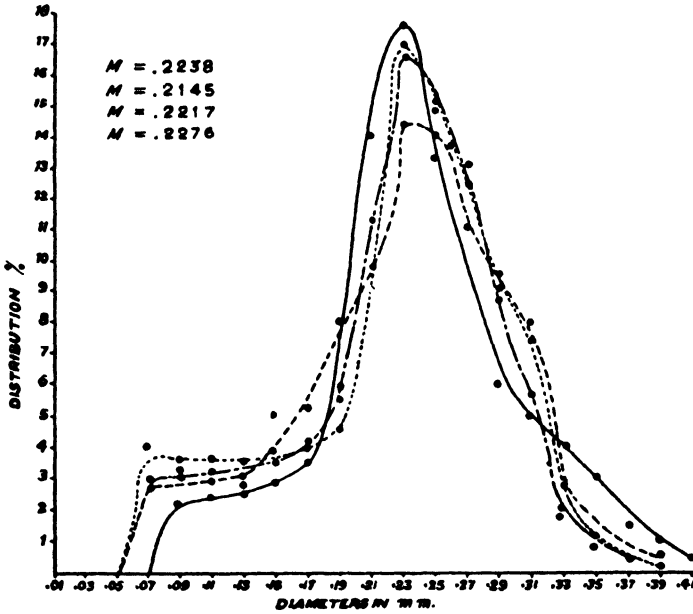



Fig. 15. Size Distribution Curves of Soil P.C. 13 Flocculated with Calcium Chloride

(M = mean diameter)

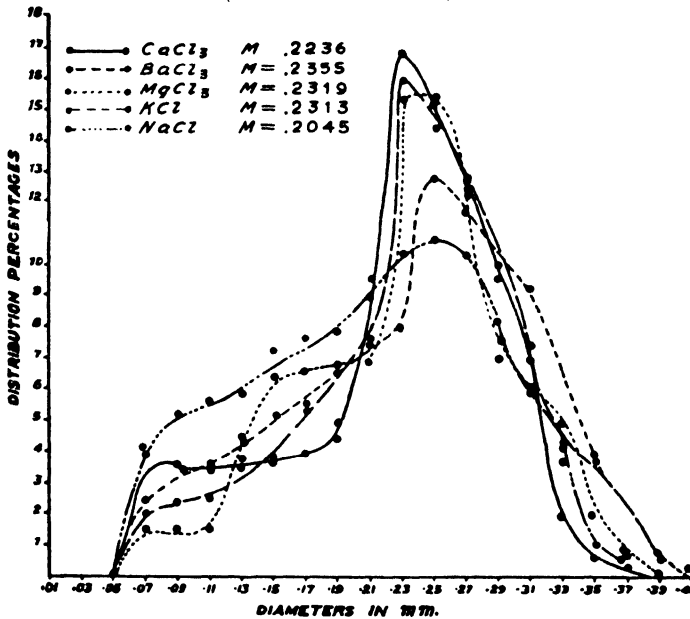



Fig. 16. Size Distribution Curves of Soil P.C. 13 Flocculated with Different Electrolytes

(M = mean diameter)

To standardize the technique of determining the floc volume of soils, preliminary studies were made of the effect of various factors, such as concentration of the clay suspension used, the nature and concentration of the flocculants employed, and the time and speed of centrifuging required to produce a compact mass of flocs.

Clay (0.002 mm) was separated from 1% soil suspensions dispersed by the HCl-NaOH method. For determining the floc volume 4 cc of the clay suspension was always used. The chlorides of Ca, Ba and Al were found to be about equally effective as flocculants and 1 cc of 0.25 normal solution was found to be enough even in the case of very clayey suspensions. The chlorides of alkali metals, as expected, did not cause flocculation unless much higher concentrations were employed, and even then the effect was rather slow. The centrifugal machine used consisted of an ordinary ceiling fan having the necessary attachments for holding three centrifugal tubes at a time, and could be worked at the rate of 620 rpm. The time of centrifuging was found to affect the values considerably at first, but after about half an hour no further decrease in volume took place, as maximum compaction and settling of flocs had occurred by then.

The procedure adopted for determining the floc volumes of soils was as follows: A 1% suspension was prepared, after maximum dispersion by the HCl-NaOH method and clay was pipetted off in the usual way. Four cc of the clay were put in the measuring tube, 1 cc of 0.25N $CaCl_2$ was added and the suspension was centrifuged for 30 minutes. The volume of the settled mass was read directly from the measuring tube, which was accurately calibrated up to 0.01 cc. The reliability of the values obtained by following the procedure outlined was tested on 12 soils by taking each soil in three separate lots and determining the volume of the floc in each case. The values obtained in all cases were almost identical.

Effect of pH on Floc Volume

The relation between pH, floc volume, and clay content is shown in Figures 17 and 18 for soil P.C. 13 and P.C. 245, respectively. Both the floc volume and the clay content increase with the pH value, but whereas the clay content reaches its maximum value at about pH 10.8, the floc volume at this point attains only a fraction of its maximum value. In fact, the pH-floc volume curve becomes very steep at this pH and the increase in floc volume is continued to pH 11.6, after which it becomes constant. This shows that though the dispersion of conventional clay is complete at pH 10.8, the subdivision of clay into ultra-clay is completed at about pH 11.6, as beyond this value no increase in floc volume is noticed. The relation between floc volume and ultra-clay is plotted in Figure 19.

For the same clay content, P.C. 13 soil gives a greater floc volume than does P.C. 245. The reason for this is that P.C. 13 soil is much richer in ultra-clay than P.C. 245, and therefore a given amount of clay in P.C. 13 contains a larger amount of finer particles

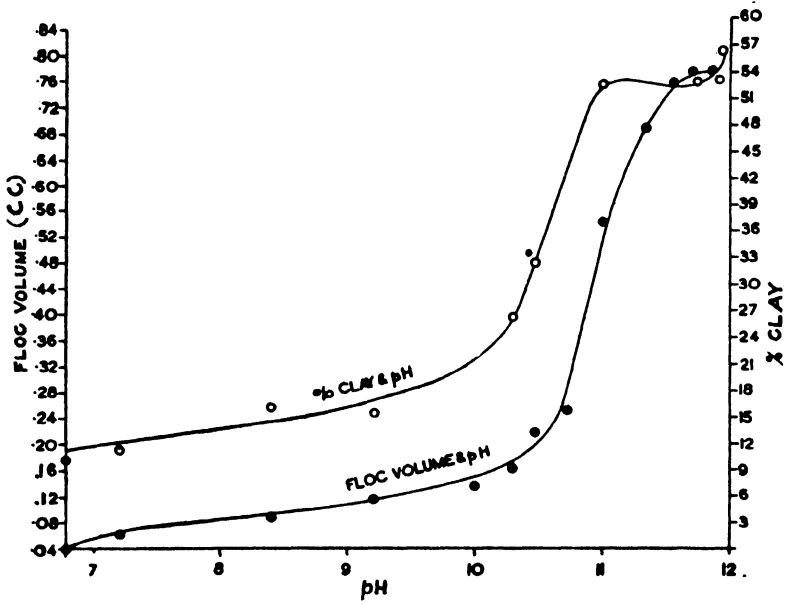



Fig. 17. Effect of pH Value on Clay Content and Floc Volume of Soil P.C. 13, Acid-Treated

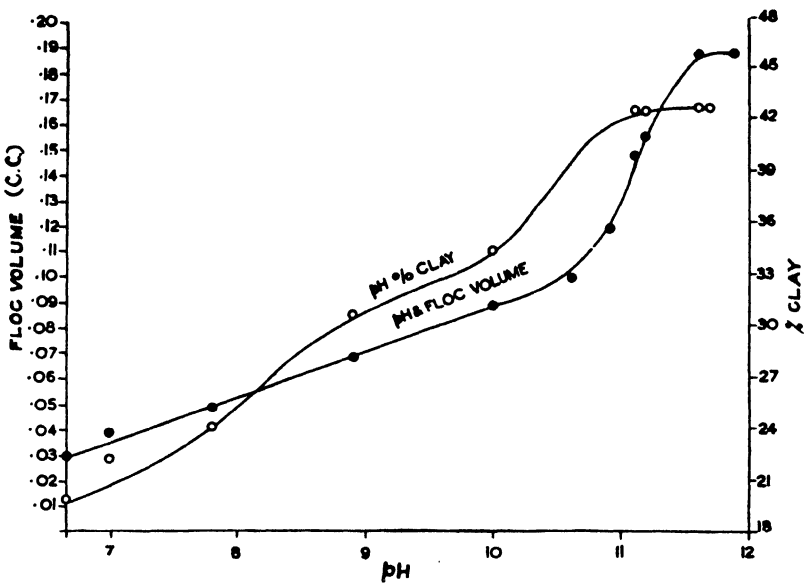



Fig. 18. Effect of pH Value on Clay Content and Floc Volume of Soil P.C. 245, Acid-Treated

than does the same amount of clay in the other soil. This obviously leads to the conclusion that size distribution in the ultra-clay region rather than the clay itself is mainly responsible for determining floc volume.

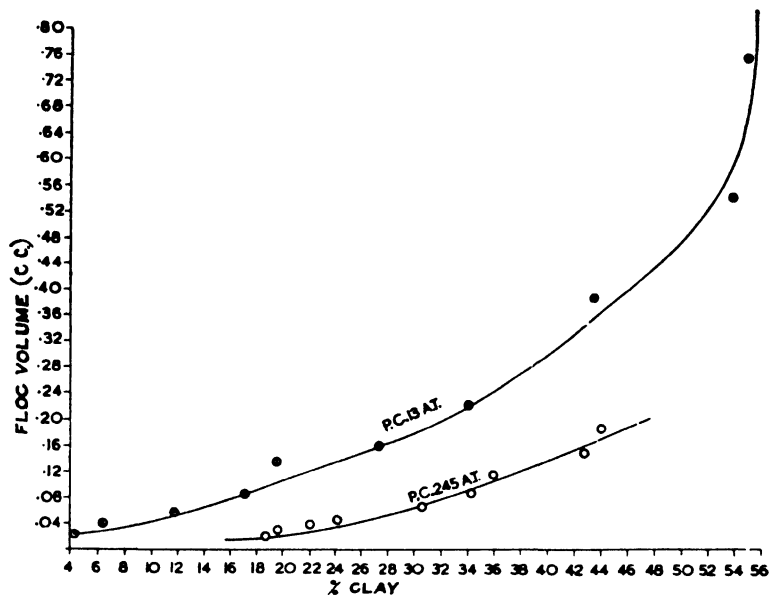



Fig. 19. Relation between Clay Percentage and Floc Volume of Soils

Table 16. Floc volume of soils when dispersed by different methods

Soil No. P.C.	Clay (.002 mm.) per cent			Ultraclay (.0001 mm.) per cent			Floc volume cc.		
	Sand method	Na_2CO_3 method	HCl-NaOH method	Sand method	Na_2CO_3 method	HCl-NaOH method	Sand method	Na_2CO_3 method	HCl-NaOH method
13	53.9	55.0	57.5	3.1	8.1	35.3	0.06	0.16	0.42
123	72.1	76.0	77.5	2.0	7.2	11.2	0.02	0.12	0.22
245	37.8	39.0	42.7	1.3	5.7	6.2	0.01	0.10	0.11

For further evidence on this point, we can disperse the soil by various methods which give the same value for conventional clay but different values for ultra-clay, as shown before. Three soils were dispersed by the HCl-NaOH method, the Na_2CO_3-NaOH method, and the sand method, respectively. The values for clay (0.002 mm), ultra-clay (0.0001 mm), and the floc volumes are given in Table 16.

Although the clay content is almost the same in every soil, irrespective of the method of dispersion, floc volume is different, and so is ultra-clay. As the latter increases when the soil is dispersed by the acid treatment, so does the floc volume. The discrepancy in the values of floc volume for the same values of clay content is so great that it is useless to attempt any correlation between conven-

tional clay and floc volume. It will be noticed also that the sand method is the least effective in dispersing ultra-clay. This confirms the view already elaborated that dispersion of clay is essentially a chemical phenomenon associated with the formation of Na saloid. As such it is akin to the well known solubility of Na salts in water. The mechanical hammer action of coarse sand has no effect on ultra-clay particles, which are too fine to receive its impact.

It is clear from this that the idea that clay particles have a colloidal coating is untenable. Colloidal particles have a separate, independent existence, and when fully dispersed they exist as ultimate units possessing measurable sizes. When they exist as aggregates, there are gaps between them, through which chemicals take a long time to penetrate; therefore reactions are slow and may take several days to come to equilibrium. But when these aggregates are broken down to their ultimate units, there is no evidence to show that their chemical reactivity or other physico-chemical properties, like moisture absorption, cohesion, etc., are due to the capillary structure of the surface of the particles. In other words, the total surface can be calculated from the diameter of the particles by simple geometry, and no correction is needed by virtue of their having a larger surface than that indicated by their diameter. This point will be dealt with more fully later.

Effect of Aging

During the course of these studies it was noticed that floc volumes of suspensions increased on standing. This may be due to the gradual increase in the dispersion of ultra-clay or to something that goes by the name of "aging", which is merely an expression without any precise meaning beyond stating the fact that some property changed with time. The effect of aging was studied on two soils, P.C. 13 and P.C. 142.

To 5-gram portions of acid-treated soils, varying quantities of NaOH were added and the suspensions were shaken for 24 hours in a mechanical shaker. They were then diluted to 500 cc to give a 1% suspension, and their pH values were determined by means of the glass electrode. Thereafter the floc volume, clay content (0.002 mm) and percentage of ultra-clay particles (0.0001 mm) were obtained. The determination of these values and of the pH values of all the suspensions was repeated after varying intervals of time. The results are given in Table 17.

The following conclusions may be drawn. As far as conventional clay is concerned, the various suspensions at different pH values acquire stable structure soon after 24 hours' mechanical shaking, for no appreciable increase in clay content is noticed up to 7 days' standing. Furthermore, the maximum dispersion on the basis of conventional clay is attained at pH 10.8 to 11.0.

The ultra-clay (0.0001 mm), however, continues to increase in all

cases up to 65 hours' standing, reckoned from the end of the 24 hours' mechanical shaking. This happens even in suspensions at pH values higher than 11, though the effect is less pronounced. This shows that ultra-clay requires not only higher pH values than 10.8 but also a longer shaking time than the usual 24 hours for complete

Table 17. Effect of aging of soil suspension*

SUSPENSION NUMBER	0.1N NaOH added	pH					FLOC VOLUME					CLAY CONTENT					PARTICLES UP TO 0.0001 MM.†			
		2 hours	26 hours	65 hours	90 hours	7 days	2 hours	26 hours	65 hours	90 hours	7 days	2 hours	26 hours	65 hours	90 hours	7 days	26 hours	65 hours	90 hours	7 days
	cc.						cc.	cc.	cc.	cc.	cc.	%	%	%	%	%	%	%	%	
										Soil P. C. 13 A. T.										
1	0.5	7.1	7.05	6.95	6.95	6.95	0.05	0.07	0.08	0.08	0.08	9.8	10.5	11.2	11.4	11.4	3.4	4.7	5.3	5.4
2	1.5	7.3	7.10	7.10	7.1	7.1	0.08	0.09	0.12	0.12	0.12	30.1	32.2	33.0	33.0	33.1	5.6	8.6	9.7	9.8
3	2.0	9.0	8.40	8.3	8.3	8.3	0.20	0.30	0.41	0.43	0.43	40.2	43.2	43.1	44.0	44.2	17.1	26.3	27.2	27.3
4	3.0	10.3	9.40	9.3	9.3	9.3	0.30	0.42	0.49	0.50	0.50	58.8	59.0	60.1	60.2	60.2	25.1	29.8	30.1	30.1
5	4.0	10.7	9.7	9.6	9.5	9.5	0.48	0.65	0.70	0.70	0.70	64.0	63.5	63.6	63.8	64.0	32.1	36.5	36.5	36.6
6	5.0	11.0	10.0	9.9	9.8	9.8	0.55	0.70	0.72	0.73	0.73	64.0	64.0	64.2	64.2	64.3	34.1	38.2	38.5	38.7
7	6.0	11.4	10.35	10.2	10.2	10.2	0.65	0.73	0.73	0.74	0.74	64.0	64.8	65.0	65.1	65.1	36.1	38.3	38.8	38.8
8	7.0	11.5	10.35	10.2	10.2	10.2	0.70	0.76	0.76	0.76	0.76	64.8	64.8	65.1	65.2	65.2	37.1	39.1	39.2	39.8
9	8.0	11.6	10.35	10.3	10.2	10.2	0.71	0.76	0.76	0.76	0.76	64.6	65.0	64.8	65.2	64.8	37.2	39.3	40.0	40.1
										Soil P. C. 142 A. T.										
1	0.5	7.0	6.90	6.85	6.80	6.80	0.05	0.07	0.08	0.08	0.08	12.1	12.3	12.5	12.7	13.0	4.1	5.0	5.1	5.1
2	1.5	7.6	7.5	8.4	7.3	7.3	0.09	0.12	0.13	0.13	0.13	25.7	26.1	26.7	26.8	26.8	6.8	8.2	8.8	9.6
3	2.0	8.8	8.3	8.2	8.1	8.1	0.20	0.32	0.39	0.41	0.41	40.2	40.3	40.2	40.3	40.3	16.1	17.1	25.1	25.5
4	3.0	9.2	9.0	8.9	8.8	8.8	0.28	0.38	0.46	0.48	0.48	50.1	51.1	51.3	52.0	52.0	20.1	23.1	28.1	28.1
5	4.0	10.8	9.9	9.7	9.7	9.7	0.57	0.62	0.63	0.63	0.63	62.0	62.1	61.9	62.3	62.5	28.1	30.1	31.1	31.2
6	5.0	11.0	10.1	10.0	9.55	9.55	0.61	0.65	0.65	0.66	0.66	62.8	62.4	62.5	63.0	63.0	30.0	31.2	31.2	31.2
7	6.0	11.2	11.1	10.0	9.55	9.55	0.65	0.68	0.69	0.69	0.69	63.2	63.5	63.5	63.6	63.6	32.0	33.0	33.0	33.1
8	7.0	11.4	10.3	10.2	10.1	10.1	0.65	0.69	0.70	0.70	0.70	63.2	63.1	63.2	63.2	63.1	33.2	33.9	34.0	34.1
9	8.0	11.5	10.5	10.2	10.1	10.1	0.66	0.69	0.70	0.70	0.70	63.0	63.0	63.1	63.1	63.2	34.1	34.6	34.2	34.2

*The time of shaking, 24 hours, is not included.

†As 24 hours' settling time is required to allow pipetting from the minimum depth of 1 mm., the value for 2 hours could not be obtained.

dispersion. This will be readily understood if we assume that dispersion of soil takes place gradually, the coarser particles being resolved first, followed by the particles in the clay region, and then by those in the ultra-clay region. After about 90 hours (including 24 hours of shaking) complete dispersion has taken place on the basis not only of conventional clay but also of ultimate primary particles in the truly colloidal region. Keeping the suspensions for a longer time than this does not produce any further change in ultra-clay, and the suspensions acquire a comparatively permanent stable state.

The floc volume, like ultra-clay content, increases with time of standing. The increase continues for as long as 65 hours in sus-

pensions at lower pH values, but for only 26 hours in more alkaline suspensions, although ultra-clay in the latter case increases to a small degree up to 65 hours. This apparent discrepancy will be readily resolved by reference to Figure 5, in which the effect of concentration of ultra-clay on the floc volume tends to become constant.

The pH value continues to decrease with time in all cases until it also becomes constant. This usually happens after 65 hours of standing, though the rate of fall gradually decreases. The explanation for the fall of pH value with time is that the reaction between alkali and the acidoid takes place very slowly, as the soil particles exist in aggregates and the reactions involved take place only at the surface. When these aggregates, on contact with alkali, are gradually resolved, first into smaller aggregates and then into ultimate primary units, fresh surfaces become exposed and the reaction continues if enough alkali is present. This will continue until hydrogen in the acidoid is completely replaced by sodium. No further fall in pH value will then take place. As the maximum dispersion can occur only when the acidoid is completely converted into Na saloid, the ultra-clay particles continue to increase with the progressive neutralization of the acidoid, and attain constant value only when sufficient alkali is kept in contact with the acidoid long enough to complete this reaction.

Contribution of Particles of Various Sizes to Floc Volume

Although it appears that ultra-clay particles determine to a large extent the volume of the flocculated mass, it is of interest to find out whether coarser particles also make a contribution to this value and if so, what the magnitude of this contribution is and at what particle size it begins.

Two H soils, with differently shaped size-distribution curves, were selected and dispersed by the addition of NaOH to raise their pH value to 11.0 and by shaking mechanically for 48 hours. Particles of various sizes were pipetted after appropriate times of settling and their floc volumes as well as their summation percentages were determined in the usual way. The results showed that particles coarser than 0.0001 mm (10^{-5}cm) do not make any material contribution to the floc volume. Particles finer than this, however, begin to affect this value to an increasing degree. It is interesting to note that although P.C. 13 contains only 27% of particles below 0.00004 mm, these particles contribute 90 per cent to the floc volume.

In order to determine the floc volume of any silica that might have gone into solution as a result of alkalinity of the medium, the two suspensions were filtered by means of Houston's pump and the floc volumes measured in the usual way by the addition of 1 cc of 0.25N $CaCl_2$ to 4 cc of the filtrates. The flocculated mass was found to be absent altogether in P.C. 149. It had a negligibly small volume in P.C. 13 because of the presence of humus.

Effect of Concentration of Suspension on Floc Volume

In order to study the effect of concentration on floc volume, four typical acid-treated soils were fully dispersed and clay was pipetted off in the usual way from 1% suspensions. Different dilutions of each clay were prepared by taking 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4 cc of the suspension and making up to a volume of 4 cc in each case with water. The floc volumes were determined as usual. The results are plotted in Figure 20: 100% concentration represents

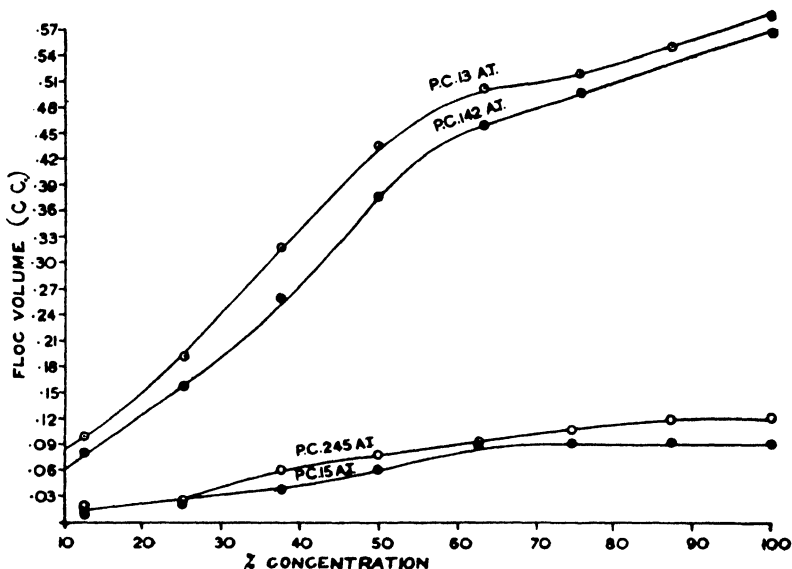



Fig. 20. Effect of Concentration of Clay on Floc Volume of Soils

original clay without any dilution, 50% represents the original clay diluted half and half with water, and so on. It will be seen from the results that floc volume does not increase in the same proportion as the concentration, and that at a certain stage it becomes constant and quite independent of the concentration. This fact may be attributed to the mutual compression caused by the particles. As the concentration of the suspension increases, the force of compression also increases because of the larger number of particles occupying the same space.

In Figures 21-23 the same results are plotted on the basis of the three ultra-clay sizes (0.0001, 0.000064 and 0.00004 mm). The values plotted along the abscissas were obtained by dividing the percentages of various sizes actually present in the soil by the number of times the clay was diluted. it will be seen that after a certain concentration of ultra-clay particles is reached, the floc volume becomes constant.

Furthermore, all four curves for each of the three particle sizes have similar shapes. That all four curves for any particle size are not superimposed is to be expected, as it has already been

shown that particles larger than 0.0001 mm do not contribute to the floc volume. When any two soils contain the same summation per-

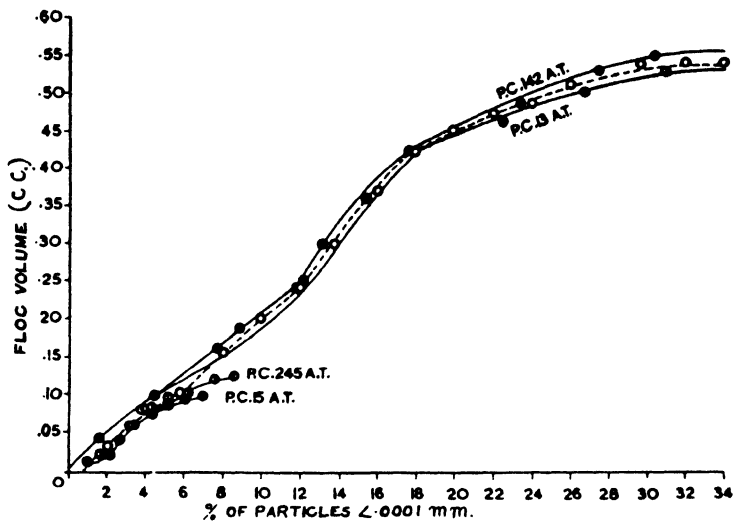



Fig. 21. Relation between Floc Volume of Soils and Percentage of Particles <0.0001 mm

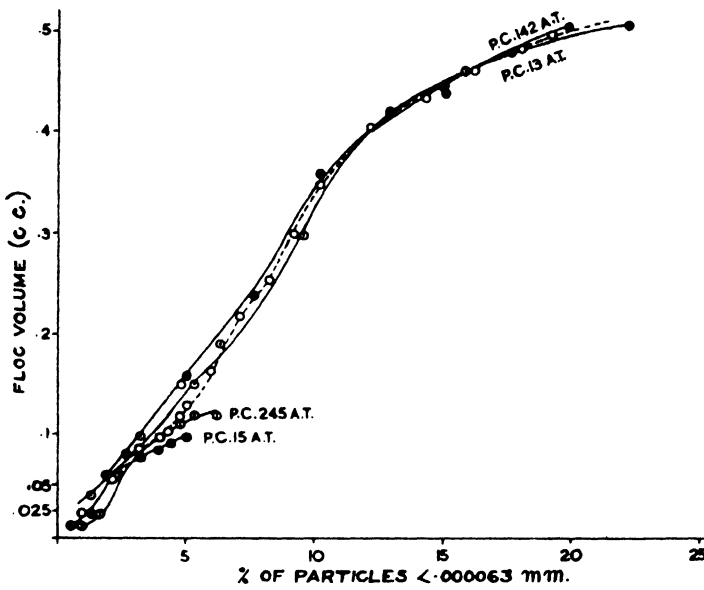



Fig. 22. Relation between Floc Volume of Soils and Percentage of Particles <0.000063 mm

centage of particles of 0.0001 mm diameter, it does not necessarily imply that their size distribution curves for various fractions be-

low this size will be alike. The dotted curve in each figure was obtained by plotting mean values of ultra-clay particles corresponding to various floc volumes. The mean curves may be used in calculating the percentages of various ultra-clay particle sizes present in a suspension.

Ultra-Clay Particles as Determined from Floc Volumes

Although it is not possible to determine with absolute accuracy, from knowledge of floc volume, the percentages of various fractions in the ultra-clay region, a number of soils were studied to discover the degree of accuracy that can be attained. A method that would

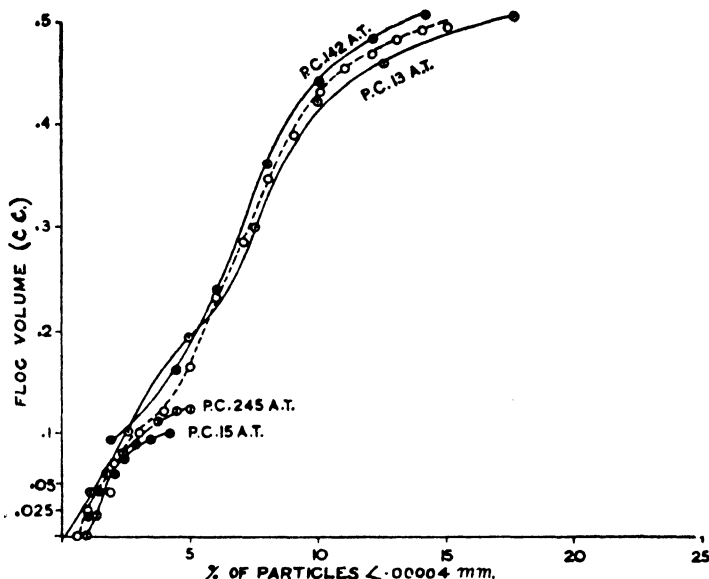



Fig. 23. Relation between Floc Volume of Soils and Percentage of Particles <0.00004 mm

give readily within a few hours a fairly if not absolutely accurate measure of the percentages of particles of such fine dimensions as 0.000063 mm obviously would be very helpful.

For this study, mean values of percentages of particles of various sizes (0.0001, 0.000063, and 0.00004 mm) corresponding to different values of flocculated volume were obtained from the mean curves plotted in Figures 21, 22, and 23. All that need be done then is to find the floc volume of a soil by the method outlined at the beginning of this chapter, i.e., take 4 cc of clay separated from 1% of fully dispersed soil suspension and determine its floc volume on the addition of 1 cc of 0.25N $CaCl_2$, followed by centrifuging for half an hour. The percentages of particles of various sizes can then be

read by reference to the mean values.

This method was tested on 63 soils. The percentages of particles of all three sizes as determined by the micropipette technique and by the proposed method, agreed fairly closely. Results with a few soils are given in Table 18 by way of illustration.

Table 18. Ultraclay as determined by the pipette method and by the floc volume method

SOIL NUMBER	FLOC VOLUME	ULTRACLAY					
		$<10^{-5}$ cm. (0.0001 mm.)		$<10^{-5.2}$ cm. (0.000063 mm.)		$<10^{-5.4}$ cm. (0.00004 mm.)	
		Pipette method	Flocculated volume method	Pipette method	Flocculated volume method	Pipette method	Flocculated volume method
	cc.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
116	0.11	6.9	6.0	4.0	4.35	3.1	3.5
117	0.04	3.2	2.37	1.7	1.50	1.2	1.30
118	0.15	8.3	7.87	5.2	5.60	4.5	4.27
119	0.38	20.2	16.3	11.4	11.0	9.1	8.8
120	0.06	4.0	3.25	2.5	2.15	2.0	1.80
121	0.05	3.6	2.80	2.5	1.80	1.7	1.50
122	0.04	3.0	2.37	1.6	1.50	1.3	1.30
124	0.04	2.9	2.37	1.5	1.50	1.4	1.30
125	0.06	4.5	3.25	2.5	2.15	1.8	1.80
126	0.22	11.3	11.00	7.4	7.10	6.1	5.75
127	0.18	10.0	9.12	6.0	6.32	4.9	5.25
128	0.08	6.2	4.06	2.5	2.80	2.2	2.20
129	0.26	13.3	12.5	8.7	8.12	6.8	6.50
130	0.23	10.8	11.50	7.5	7.36	6.0	5.92

Thus the ultra-clay fractions can be determined with a fair degree of accuracy by the proposed method. As no particular skill on the part of the observer is involved and determinations of such fine particles in a number of soils can be made within a few hours, the method has much to be said in its favor.

CHAPTER XII

MECHANICAL ANALYSIS OF FERROALUMINOSILICATES

It is of considerable interest to know if the ferroaluminosilicates prepared in the laboratory behave like soils as regards mechanical analysis. We have already seen that, barring certain constitutional differences which are only natural in view of their manner of production (which is disintegration in the case of soils and integration in the case of artificial aluminosilicates), ferroaluminosilicates behave exactly like soils in most of their physico-chemical reactions. There is no reason to suppose that mechanical analysis of silicates would not conform to the same general pattern associated with soils.

Mixtures of varying silica, alumina and ferric oxide ratios were prepared by adding solutions of different concentrations of ferric and aluminum silicate. The precipitates were washed over Buchner funnels with 0.05N HCl to remove unreacted sodium silicate and other extraneous cations, if any, then with distilled water until free from chloride ions, and finally with alcohol. The precipitates were then dried. The chemical composition of the mixtures as determined by the usual methods of analysis is given in Table 19.

In order to find a suitable method for dispersing ferroaluminosilicates, the following methods often used in soil analysis were tried on one of the mixtures:

(1) Shaking the suspension for 24 hours in a mechanical shaker with enough NaOH to raise the pH value to 10.8.

(2) Wet-grinding the mixture with a rubber pestle and subsequent shaking for 24 hours in a mechanical shaker.

(3) Same as (2) but enough NaOH added to raise the pH value to 10.8 before shaking.

(4) Shaking for 24 hours with coarse sand (1 mm diameter) to the amount of fivefold the weight of the sample.

(5) Same as (4) but enough NaOH added to bring the pH value to 10.8 before shaking.

The results of mechanical analysis, determined by means of the Chaino-hydrometer are given in Table 20. Methods 1, 3 and 5 are about equally efficient, whereas the purely mechanical methods 2 and 4 do not produce maximum dispersion but give a state of aggregation which is the same in both cases.

It has been shown that various methods of soil dispersion which are equally efficient if reckoned on the basis of conventional clay (0.002 mm) may give entirely different size distributions in the ultra-clay region. In order, therefore, to determine how these three methods compare as far as dispersion of ultra-clay is concerned, the suspensions obtained by methods 1, 3 and 5 were subjected to

Table 19. Chemical analysis of ferroaluminosilicate mixtures*

MIXTURE NUMBER	Fe_2O_3	Al_2O_3	SiO_2	$\frac{SiO_2}{Fe_2O_3 + Al_2O_3}$
	per cent	*per cent*	*per cent*	
1	19.3	0.00	55.7	2.89
2	13.7	3.2	55.5	3.28
3	11.3	6.3	57.2	3.25
4	9.7	8.3	58.4	3.25
5	9.5	8.7	59.8	3.28
6	9.4	9.6	62.5	3.29
7	5.4	11.3	66.3	3.97
8	3.3	13.9	71.2	4.14
9	0.0	15.4	76.0	4.94

*The difference between 100 per cent and the total constituents of each mixture is due to water of hydration.

Table 20. Mechanical analysis of ferroaluminosilicate mixture 4 dispersed by various methods

METHOD OF DISPERSION*	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES				
	0.06 mm.	0.02 mm.	0.01 mm.	0.005 mm.	0.002 mm.
1	78.4	43.9	28.2	17.2	14.15
2	83.9	44.05	7.6	6.8	2.1
3	73.1	45.1	31.1	17.9	14.7
4	85.5	44.0	8.0	7.1	1.75
5	76.0	44.0	32.7	27.6	16.90

* See text for description of methods.

ultramechanical analysis by the micropipette technique. The results given in Table 21 show clearly that method 3 is the most efficient. The total dispersion in the ultra-clay region, however, is still very low.

For silicate mixtures we find that the chemical method of dispersion is successful only when some preliminary mechanical treatment such as grinding with a rubber pestle has been given. Soils, on the other hand, disperse to the maximum degree when they are merely left in contact with water containing enough NaOH to raise their pH values to 10.8. No subsequent shaking and no preliminary

mechanical treatment are needed. This is shown by the results in Table 22, which were obtained by dispersing an acid-treated soil by shaking with NaOH at pH 10.8 with and without preliminary grinding with a rubber pestle. The two sets of values for various ultra-clay fractions are almost identical.

Table 21. Ultramechanical analysis of mixture 4 dispersed by various methods

METHOD OF DISPERSION*	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES		
	0.001 mm.	0.00063 mm.	0.00025 mm.
1	0.0	0.0	0.0
2	1.9	0.8	0.0
3	4.4	3.6	2.1

*See text for description of methods.

Table 22. Effect of preliminary grinding on ultramechanical analysis of soil P. C. 13

TREATMENT	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES					
	0.002 mm.	0.001 mm.	0.00025 mm.	0.0001 mm.	0.000063 mm.	0.00004 mm.
No preliminary mechanical treatment	59.2	58.6	50.2	45.8	36.8	26.4
Preliminary treatment with rubber pestle	59.7	57.8	50.6	46.4	36.2	25.7

This difference in the two cases is probably due to the fact that the mixtures of the silicates prepared in the laboratory have not undergone natural disintegration and weathering as have the soils. In fact, grinding with a rubber pestle as a preliminary mechanical treatment may not be sufficiently drastic to put these mixtures on the same footing as natural soils.

A more drastic mechanical treatment--grinding in a colloid mill--was also tried on the mixtures of silicates. The colloid mill was a mechanically driven agate pestle and mortar which gave efficient and thorough grinding of the material. The time of grinding required for the maximum effect was determined by taking a 5-gram portion of a mixture, working it into a thin paste with water, and subjecting it to the action of the colloid mill for various intervals of time. The ground material, in each case, was transferred to a separate bottle and shaken with the requisite amount of alkali for 24 hours, as

usual. The results (Table 23) show that 1 hour of grinding is required to produce the maximum effect. Further grinding does not increase the dispersion.

The various mixtures were then dispersed by rubbing with a rubber pestle and by grinding in a colloid mill for 1 hour as mechanical treatments preliminary to chemical dispersion (shaking with NaOH at pH 10.8), and were subjected to complete mechanical and ultra-mechanical analysis (Tables 24 and 25).

Another set of each of these mixtures was subjected to grinding in a colloid mill for 1 hour and air-dried. They were redispersed by grinding with a rubber pestle followed by shaking with NaOH for 24 hours. The results of the mechanical analysis are included in Table 25.

Table 23. Effect of time of grinding in a colloid mill upon dispersion of silicate mixture 4

TIME OF GRINDING	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES						
	0.01 mm.	0.005 mm.	0.002 mm.	0.001 mm.	0.00025 mm.	0.0001 mm.	0.000063 mm.
minutes							
15	61.4	45.2	27.3	20.3	8.1	5.1	1.9
30	67.3	51.4	33.6	23.5	9.3	7.2	3.2
60	77.9	66.5	49.9	32.8	12.9	10.3	4.1
120	76.5	67.2	48.5	31.7	12.1	9.8	3.5

Comparison of the results in Table 24 with those in the upper rows of the different mixtures shows that preliminary grinding in a colloid mill produces far more clay than does rubbing with a rubber pestle. Furthermore, the figures in Table 25 for mixtures subjected to mill grinding as the only preliminary mechanical treatment differ considerably from the figures in the same table for mixtures subjected also to air-drying and regrinding with a rubber pestle. This is evidently because grinding breaks down the aggregates into smaller particles which remain as such in the wet state, but recombine on drying to form crumbs again.

It will be seen from Table 25 that the first four mixtures have approximately the same mechanical composition and the same amount of clay and ultra-clay fractions. The succeeding mixtures contain decreasing amounts of clay as well as of ultra-clay particles. The differences, however, are probably only apparent. As shown in Table 19, the mixtures are numbered in the order of decreasing amounts of iron and increasing amounts of Al. It appears that when the Al content of a mixture increases beyond a certain limit, partial dissolution of aluminum silicate takes place in the alkaline solution. This causes partial coagulation of the suspension, which is reflected in low values of the clay and ultra-clay fractions. As the Al content of a mixture increases further, the dissolution and there-

Table 24. Mechanical analysis of silicates dispersed by grinding with a rubber pestle and shaking with alkali at pH 10.8

MIXTURE NUMBER	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES								
	0.06 mm.	0.02 mm	0.01 mm.	0.005 mm.	0.002 mm.	0.001 mm.	0.00063 mm.	0.00025 mm.	0.0001 mm.
1	75.2	48.8	24.5	19.9	16.5	5.5	3.9	2.3	1.5
2	75.9	37.2	23.5	20.7	16.3	4.4	3.6	2.0	1.3
3	75.9	37.2	28.7	17.3	13.5	4.9	3.7	2.3	1.7
4	74.1	44.9	41.6	17.9	14.3	4.7	3.6	2.1	1.7
5	74.5	44.3	39.9	16.7	12.3	3.7	2.3	1.5	0.7
6	78.7	49.8	30.6	16.9	12.1	2.5	1.5	0.8	0.6
7	77.9	50.8	32.3	15.3	10.5	2.3	1.0	0.6	0.2
8	79.3	51.2	33.6	12.7	7.8	2.1	1.2	0.8	0.5
9	83.4	53.6	33.9	11.5	8.4	2.3	1.0	0.8	0.5

Table 25. Mechanical analysis of silicates dispersed by grinding in a colloid mill and subsequent shaking with NaOH*

MIXTURE NUMBER	SUMMATION PERCENTAGES OF PARTICLES OF VARIOUS SIZES									
	0.06 mm.	0 02 mm.	0.01 mm.	0.005 mm.	0.002 mm.	0.001 mm.	0.00063 mm.	0.00025 mm.	0.0001 mm.	0.000063 mm.
1	82.1	75.3	72.3	71.1	53.4	38.4	....	18.3	12.3	5.6
	79.3	62.5	49.2	46.6	33.7	13.2	8.5	5.9	4.9	2.1
2	82.9	77.4	72.9	71.5	51.3	36.5	23.5	16.2	9.7	4.2
	80.4	65.3	51.3	43.3	32.2	13.1	7.6	5.4	3.9	1.5
3	85.3	78.0	75.9	70.8	48.7	34.1	21.2	13.5	9.3	4.1
	81.9	65.9	53.5	42.9	31.9	13.1	6.3	4.9	3.8	1.2
4	85.9	79.3	78.3	67.3	49.1	32.1	20.9	12.1	9.5	3.6
	83.5	67.7	53.3	42.1	30.1	11.4	6.3	4.5	2.9	1.6
5	87.3	78.4	78.3	....	46.2	30.1	19.5	10.6	8.6	3.6
	84.3	67.9	55.9	40.3	30.4	8.5	4.2	3.3	2.7	0.7
6	87.4	84.5	76.6	66.9	43.0	24.1	15.3	10.3	8.2	2.9
	85.9	71.3	58.6	39.7	28.1	8.3	3.3	3.2	2.1	0.00
7	93.6	83.9	79.6	65.3	42.9	22.2	17.6	9.6	8.1	2.3
	87.6	72.3	59.6	38.2	26.2	8.4	2.2	2.9	2.1	0.5
8	97.4	85.6	80.3	65.4	39.9	19.3	16.4	9.4	6.7	2.2
	88.5	73.6	61.9	39.1	24.3	6.9	2.4	2.8	1.9	0.6
9	98.1	85.9	83.9	54.3	38.5	19.5	16.2	9.2	5.3	1.9
	88.6	73.9	62.3	37.2	20.1	6.2	2.1	2.1	1.8	0.4

* The values in the lower row for each mixture were obtained by air-drying the mill-ground material and then dispersing it by means of the rubber pestle treatment before shaking with alkali.

fore the coagulation effects become more and more pronounced, resulting in further lowering of the values of clay and ultra-clay fractions. As iron silicate resists the dissolution action of alkali, no such effect is noticed in mixtures rich in iron.

In soils no such dissolution of Al takes place as long as the quantity of alkali added is not appreciably large, and the pH value does not rise much beyond 11. In fact, soils rich in Al yield fairly stable suspensions. This is easily understood when it is remembered that Fe and Al are easily accessible to acids and alkalies in artificial silicates, whereas in natural soils only the portion constituting the surface can be attacked. A confirmation of this view is furnished by the fact that if a number of H soils are shaken with 0.1N HCl,

Table 26. Relation between the sesquioxides dissolved from a H-soil by 0.1N HCl and acid displaced by a neutral salt

Soil No.	Exchange acidity m.e. per 10 gm.	Sesquioxides m.e. per 10 gm.
A.T. 1	1.64	1.85
A.T. 2	0.90	0.88
A.T. 3	0.86	0.92
A.T. 15	0.65	0.40
A.T. 16	1.70	1.68
A.T. 17	1.50	1.20
A.T. 23	4.40	4.00
A.T. 24	4.40	4.80

the amount of Al and Fe brought into solution is almost equivalent to the acid displaced by shaking the soil with a neutral salt. This will be clear from Table 26.

As the method of finding exchange acidity as well as the procedure of shaking with 0.1N acid are purely arbitrary, these results cannot be taken too seriously beyond the fact that they do support the view that in natural soils only that portion of the sesquioxides is attacked by acid which constitutes the surface. The portion forming the bulk of the rest of the soil is inaccessible.

Soils are known to be completely dispersed at pH 10.8. At lower pH values, the dispersion is small and any rise in pH value gradually causes increased dispersion.

To determine the dispersion of silicates at various pH values, four mixtures were given preliminary treatment with a rubber pestle, and their 1% suspensions were prepared. The clay content (0.002 mm) was determined by means of the Chaino-hydrometer in each case on the gradual addition of increasing amounts of NaOH. After each addition of NaOH the suspensions were put aside for 48 hours (with occasional shaking by hand) before the clay percentage was determined. The pH values of the suspensions were also noted at the same time by means of the glass electrode. The results are plotted in Figure 24. Dispersions of an acid-treated soil at different pH values determined in the same manner as in the case of the silicate mixtures behave similarly as far as dispersion is concerned. Just as dispersion in soils increases gradually with a rise in pH

value and reaches a maximum at pH 10.8 to 11.0, so dispersion in mixtures continues to increase with the pH value to about 10, at

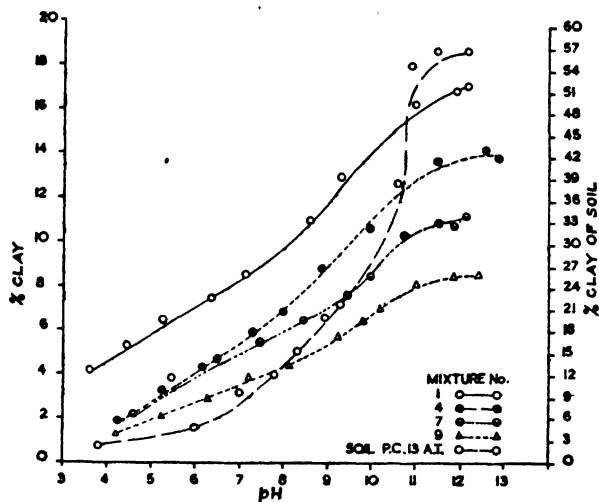



Fig. 24. Dispersion of Ferroaluminosilicates (after Grinding with a Rubber Pestle) at Different pH Values

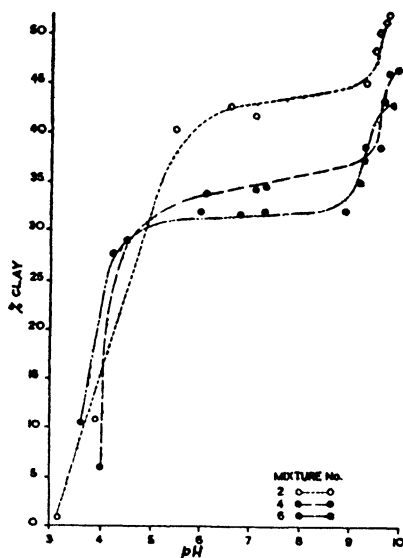



Fig. 25. Dispersion of Ferroaluminosilicates (after Grinding in Colloid Mill) at Different pH Values

which point the increase becomes more abrupt and is continued until the maximum value of clay is attained at about pH 11.

The dispersion of silicates at different pH values after grinding in a colloid mill is shown in Figure 25.

The curves are steeper and the maximum values for clay content are obtained at much lower pH values than when the grinding is done with a rubber pestle. This shows that when the chemical method of dispersion is aided by such drastic mechanical methods as grinding in a colloid mill for 1 hour, the maximum dispersion is brought about much sooner. In other words, the effects of chemical and mechanical dispersion are additive. But it will be readily seen that grinding in a colloid mill alone, however drastic this treatment may be, cannot produce any marked dispersion: addition of alkali is essential.

CHAPTER XIII

MOVEMENT OF PARTICLES IN SEDIMENTING COLUMNS

All methods of mechanical analysis of soils depend on the laws governing the movement of particles in sedimenting columns. Stokes' law applies to the movements of very fine particles where the motion is so slow that terms involving the square of the velocity can be easily neglected. Under such conditions it is assumed that the motion of particles is governed purely by laws of viscous flow and that the inertia of the fluid does not affect their movements. It has been shown that this assumption is justified only when the diameter of the falling particle is such that

$$\frac{vdp}{\eta} < 1$$

where v is the velocity and d the diameter of the falling particle, while p is the density and η the viscosity of the medium in which the particle falls. The quantity $\frac{vdp}{\eta}$ is known as Reynolds' number (R) and it obviously increases with particles of larger diameters and higher velocities.

When for a given diameter, Reynolds' number exceeds unity, the inertia terms cannot be neglected, i.e., the force resisting its motion will now depend upon the inertia of the fluid as well; in other words, the real diameter of the particle will be greater than that calculated by Stokes' formula. If water (at 30^{0} C) is used as the settling medium, the value of R will exceed unity when the diameter of the falling particle is larger than 0.075 mm. As sand particles are much coarser than this, they can be graded by the method of sedimentation only if necessary corrections are applied to the diameters calculated by Stokes' formula.

Knowing Reynolds' number, the necessary correction to be applied to the Stokes' diameter can be calculated according to Goldstein or Zahm. Goldstein obtained his function theoretically whereas Zahm's was obtained from the results of experiments.

Zahm's function has been used in the mechanical analysis of canal silts and sands by means of the siltometer, described previously. In the Puri siltometer the sand particles are graded by allowing

them to fall through a long column (200 cm) of water and collecting the fractions in separate boxes that move in position under the water column at predetermined intervals of time.

In the present investigation this siltometer was used throughout.

Effect of Varying the Length of the Sedimenting Column on Sand Particles

Sand samples of varying degrees of coarseness collected from the beds of the various canals were analyzed in the Puri siltometer by

Table 27. Effect of varying the length of the sedimenting column on mean diameters of sands.
Diameter of both tubes = 2.5″.
Mean Diameters in mm.

Sample No.	Length of tube= 200 cm.	Length of tube= 400 cm.	Sample No.	Length of tube= 200 cm.	Length of tube= 400 cm.
1.	.1574	.1492	13.	.2543	.2475
2.	.1529	.1385	14.	.2529	.2344
3.	.1501	.1347	15.	.2502	.2337
4.	.1517	.1345	16.	.3246	.3073
5.	.1520	.136	17.	.3040	.2898
6.	.2028	.1858	18.	.3018	.2752
7.	.2031	.1940	19.	.3042	.2963
8.	.2097	.1947	20.	.3016	.2737
9.	.2112	.1960	21.	.3506	.3327
10.	.2115	.1967	22.	.3566	.3284
11.	.2093	.1919	23.	.3508	.3234
12.	.2504	.2427	24.	.3513	.3464
			25.	.3527	.3374

using 200-cm and 400-cm columns of water. The mean diameters as calculated from these results (by multiplying the percentages of particles of various sizes interpolated from the summation curves with the corresponding particle size, and dividing the sum of all such products by 100) are given in Table 27. It will be seen from the values given in Table 27 that by using a longer column consistently lower values for mean diameter (M) are obtained. This is probably due to the effect of the walls of the containing vessel on the settling velocity of the particles.

The influence of the walls becomes more effective when the length of the sedimenting vessel increases, since more and more particles move along the walls as the sedimentation proceeds, and the particles which do so have little tendency to change their path. In order to verify this point several samples of sands were dropped into 90- and 200-cm columns of water contained in glass tubes of equal diameter. At the bottom, the tubes were fitted with rubber corks, each containing in the center a small glass tube of diameter nearly one-

third that of the sedimentation tube. The amount of the sample collected in this small tube was determined in each case. The results (Table 28) show that in a longer tube more particles travel along the sides of the tube, as the amount collected in the center is comparatively small. This substantiates the explanation given above for the lower value of mean diameter observed in a longer column.

Effect of the Width of the Sedimenting Column on the Movements of Particles

In order to find out the effect, if any, of the width of the sedimenting column, two brass pipes, 2.5 and 1.6 inches in diameter but having the same length (200 cm), were used one after the other in the Puri siltometer and a number of samples analyzed in each case.

The results (Table 29) clearly show that a narrower column gives a lower value for the mean diameter. This is evidently because more particles will move along the sides in a narrow pipe than in a wide one. This results in lowering their actual rate of fall.

Table 28. Effect of walls on the fall-of particles in sedimentation tubes of different lengths
(5 gm. of samples were dropped in each case.)

Sample No.	Wt. in grams falling in the tube fixed in the centre of the rubber cork.	
	Length of column = 200 cm.	Length of column = 90 cm.
1	.42	.54
2	.50	.56
3	.46	.54
4	.51	.56
5	.45	.56
6	.46	.50
7	.50	.54
8	.44	.52
9	.44	.54
10	.46	.54

Effect on the Movements of Particles of Samples of Different Weights in a Sedimenting Column

In order to study the mutual influence of particles in a sedimenting column, 10.5 and 2.5 grams of a number of samples were analyzed in the siltometer using a column 200 cm long and 1.6 inches wide. The results (Table 30) show that the value of M for any sample remains practically unchanged for samples of different weights. The effect of mutual collisions of particles, therefore, at least within the concentrations tried, is almost nil. This is what may be expected, since sand particles become separated from one another on account of their different velocities soon after being dropped.

Effect on the Movements of Sand Particles of Fine Suspended Matter in a Sedimenting Column

It has often been asserted that the presence of fine suspended matter in water will alter its viscosity. This is of practical importance in view of the fact that the rate of settling of canal silts on the bed,

for the same hydraulic data, has been found to vary with the quantity of finer particles carried in suspension. It can, however, be shown that the increase in viscosity of water charged with 8 oz of fine silt per cubic foot is equal only to that produced by about 2° C difference of temperature, and therefore it should have no material

Table 29. Effect of varying the width of the sedimenting column on mean diameters of sands.
Both tubes were 200 cm. in length

Sample	Mean diameter mm	
No.	2.5" tube	1.6" tube
1	0.3816	0.3614
2	.1996	.1894
3	.2458	.2063
4	.2894	.2652
5	.3394	.3035

effect on the rate of settling of particles, as the normal amount of suspended matter in canals rarely exceeds 2 oz per cubic foot of water.

It might be argued that though the fine suspended matter has no effect on viscosity, it may exert some direct influence on the movements of bigger particles. Silt was therefore analyzed in the siltometer using water with increasing quantities of suspended matter. The results given in Table 31 show that the mean diameter remains unaffected by the presence of fine particles.

Behavior of Silt Particles Carried in Suspension by Channels

Silt is carried in suspension by the water of a channel, and when deposited on the bed it naturally reduces the capacity of the channel. It is thus of great importance to an irrigation engineer to adjust the shape and velocity of the channel in accordance with the quantity and the size of the particles in suspension, to prevent sedimentation as far as possible. For this he should know the amount as well as the grading of the particles carried. The silt charge at a given point can be determined by taking a sample of water from that point by means of a suitable sampler and leaving it to settle for a time, drawing off the supernatent water by a syphon, evaporating the residual water and weighing the deposit. The deposit may then be graded by combining the processes of sieving and sedimentation, or by passing it through a siltometer if it is in sufficient quantity.

Table 30. Effect of dropping different weights of samples on their mean diameters.
Tube used was 200 cms. long and 1.6" in diameter.
Mean diameters in mm.

Sample No.	Weight of the sample dropped		
	10 gms.	5 gms.	2.5 gms.
1.	.1470	.1493	.1455
2.	.1394	.1425	.1412
3.	.1404	.1403	.1440
4.	.1409	.1403	.1420
5.	.1330	.1319	.1325
6.	.1794	.1820	.1809
7.	.1995	.2001	.1949
8.	.1868	.1847	.1882
9.	.1947	.1934	.1996
10.	.1923	.1946	.1957
11.	.1871	.1871	.1889
12.	.2443	.2445	.2477
13.	.2494	.2514	.2519
14.	.2389	.2450	.2372
15.	.2340	.2274	.2380
16.	.3148	.3148	.3094
17.	.2947	.2927	.2930
18.	.2804	.2760	.2796
19.	.2983	.2980	.2992
20.	.2736	.2780	.2757
21.	.3289	.3313	.3309
22.	.3324	.3420	.3464
23.	.3195	.3192	.3201
24.	.3316	.3447	.3339
25.	.3362	.3339	.3338

Table 31. Effect of suspended matter in water on the mean diameter of sand

Suspended matter gm. per liter	Mean diameter mm.
0	.3011
0.12	.2894
0.16	.2952
0.39	.2998
0.62	.3002
1.11	.3022
4.09	.2958
5.11	.2950

Various types of samplers for taking water from canals have been devised from time to time. One such instrument in use in the Punjab is known as "bottle sampler"; it consists of a long pipe attached at one end to a frame holding a one-liter bottle fitted with a rubber stopper which is operated by a lever fixed at the other end of the pipe. The mouth of the bottle is lowered to a desired depth; the stopper is lowered onto the bottle, again by working the same lever in the reverse direction. The mouth of the bottle should be kept open for the minimum time required to fill the bottle. This should be ascertained experimentally by the observer. The importance of filling the bottle as quickly as possible will be realized from the results in Table 32, which gives the total silt in suspension determined by keeping the mouth of the bottle open for varying lengths of time.

Table 32. Effect of time of sampling on the value of total silt.

Time (seconds)	Silt in gms. per litre.
12 (when just full)	.294
15	.336
20	.364
25	.378
30	.378
40	.420
50	.497
60	.518

The distribution of silt in a vertical section of a stream varies with depth both as regards quality and quantity. Its determination is of practical importance, as it gives the best bed level for a branch taking off from the main stream. It can only be ascertained by observations or by experience with similar streams. Samples were taken from vertical sections of about half a dozen channels at various points and it was found that silt charge at 0.6 of the depth was very nearly equal to the mean quantity of silt in the whole vertical column. The results of observations made on two channels are recorded in Table 33.

The results obtained on other channels were similar. The fact that the silt charge at 0.6 of the depth is nearly equal to the mean quantity of silt in the whole vertical column is of great value, since in order to find the total amount of silt carried in a certain volume of canal water, a sample from 0.6 of the depth can be taken and its silt content determined. It must be mentioned that these results of silt distribution in a vertical column refer to channels that are under controlled conditions. In the case of channels in floods or with irregular gradients or undergoing heavy silting or scouring, the phenomena of silt distribution may vary from time to time and from one channel to another.

Silt is not only carried in suspension but is also rolled along the bed of a stream. Coarse silt is more often rolled than carried, and when carried it is usually found in greater proportion near the bed. Since both the rolling and carrying powers of a channel depend upon its velocity of flow, it is quite likely that there may be some relation existing between the suspended and rolling silt. The suspended silt present at a depth near the bed, on account of its proximity to the rolling matter, will show a better relation with the latter.

Table 33.

Showing the vertical distribution of silt.

Point of Sampling	Total silt in gms. per litre.	
	Upper Chenab Canal R.D. 1000 Depth 13.5 ft.	Lower Chenab Canal R.D. 3500 Depth 14.0 ft.
.1D	.732	.735
.2D	.686	.747
.3D	.695	.774
.4D	.707	.770
.5D	.742	.788
.6D	.778	.812
.7D	.828	.873
.8D	.855	.891
.9D	.921	.924
Mean	.772	.813

In order to establish the relation between the size of silt in suspension and that rolled along the bed, suspended matter was taken at 0.8 of the depth. It was not possible to collect samples within one foot of the bed without disturbing the bed material. The depths of the channels observed varied from 5 to 8 feet. Shallower channels, less than 5 feet deep, could not be sampled from 0.8 of the depth for the reason mentioned above. Rolling matter was taken by means of a sampler consisting essentially of a scoop which digs into the bed when revolved, and a cowl, which protects the sample from being washed away when the sampler is brought to the surface. Samples of both types were taken from ten channels on different dates and graded in the Puri siltometer. The only relation found was that the maximum size present in the suspended matter was nearly equal to the mean size of the rolling silt.

CHAPTER XIV

RELATION BETWEEN MECHANICAL ANALYSIS AND THE SPECIFIC SURFACE OF SOILS

Specific surface is defined as the surface area per unit mass of the particles. For purposes of simplicity of calculation, the particles are assumed to be spherical, having an "equivalent" diameter which has the same significance as the diameter calculated from Stokes' Law in ordinary mechanical analysis by sedimentation.

In a previous chapter a micro-pipette for the ultramechanical analysis of soils was described. This method makes it possible to push the mechanical analysis of soils down to particles of 0.00004 mm diameter. As the finer particles contribute by far the most to the determination of the specific surface, it is evident that true estimation of the extent of the surface presented by the soil is possible only if the size distribution of particles in the region of ultra-clay is known. Specific surface is given by the formula:

$$SS = 0.02264 \; \Sigma \; p/d$$

where p is the percentage by weight of particles of mean diameter d.

The following discussion will make the derivation of the above formula clearer.

Let a sample of soil weighing W units be separated into fractions of different sizes. Let the weight of one of these fractions be w, its equivalent diameter d, and particle density, ρ. It is assumed that the density of each fraction is the same as the density of the whole soil. It is also assumed that particles in each fraction can be assigned an equivalent diameter from their rate of settling in water in accordance with Stokes' Law.

If the number of particles in this fraction is n and v is the volume of one sphere, we get:

$$\begin{aligned} w &= n \, . \, g \, . \, \rho \, v \\ &= n \, . \, g \, . \, \rho \times \pi \, d^3/6 \end{aligned} \qquad \text{(i)}$$

The total surface of these particles is given by:

$$S = n\,a, \text{ where } a \text{ is surface of one sphere}$$
$$= n\,\pi\,d^2 \qquad \text{(ii)}$$

Summing up for the entire sample, we get:

$$W = \Sigma\, w$$
$$= \pi\, g\, p\ \Sigma\ nd^3/6 \qquad \text{(iii)}$$
$$S = ns = \pi\,\Sigma\ nd^2 \qquad \text{(iv)}$$

If we divide (ii) by (i) we get:

$$S/w = 6/g\,p\,d \therefore S = \Sigma\ s = \frac{6}{gp}\ \Sigma\ w/d \qquad \text{(v)}$$

If M is the total mass of the sample M = W/g.

$$\text{Therefore } S/M = 6/Wp\ \Sigma\ w/d$$

Now if the given fraction forms P per cent by weight of the total sample

$$w/W = P/100$$

$$\text{Therefore } S/M = 6\ (\Sigma\ p/d)/100\cdot p$$

For soil particles it is generally assumed that $p = 2.65$.

$$\text{Therefore } S/M = (6/265)\ \Sigma\ p/d = 0.02264\ \Sigma\ p/d \ldots\ldots\ldots\ldots\ldots \text{(vi)}$$

The ratio S/M is obviously the specific surface and it can be calculated from equation (vi) if the percentage by weight of each fraction and its "equivalent diameter" is known.

Another method of representing specific surface would be to consider it in terms of unit volume, i.e., S/V

$$\text{Obviously } S/V = p.S/M = 2.65\ S/M = 0.06\ \Sigma\ p/d$$

However, in the case of soils S/M is preferable, since the mechanical analysis is in terms of weight.

The following further postulates are made in calculating specific surface by the above method:

(a) The particles of various sizes in any fraction can be replaced by spherical particles, whose diameter is the mean of the value considered to be the upper and lower limits of the size for the fraction. For instance, particles lying between 0.015 and 0.017 cm are treated as if they had a common diameter equal to 0.016 cm.

(b) When the lower limit of analysis is reached, i.e., when the particles are so fine that further analysis is not possible or is considered unnecessary, the diameter of the particles is taken to be

equal to half of the value for the diameter of the finest particles determined by analysis. Thus if there are 25% of particles whose diameters are less than 4×10^{-6} cm, the highest degree of fineness attained in some experiments, it is usual to treat this 25% as having a diameter equal to 2×10^{-6} cm.

It is evident from the above discussion that the value of specific surface would vary with the point at which further analysis is stopped. It is thus not possible to obtain its unique value unless it is with reference to some fixed lower limits of analysis. The following numerical example will show that it is really so.

Soil No. P.C. 13

Particles below 0.002 mm	=	58.8%
Particles below 0.001 mm	=	57.8
Particles below 0.00063 mm	=	54.6
Particles below 0.00004 mm	=	26.4

If the analysis were stopped at 0.002 mm, the contribution of the particles below this size to the specific surface according to the above postulates would be

$$S_1 = 0.02264 \times \frac{58.8}{1/2 \times .002/100} \text{ sq cm/gm}$$

$$= 1.33 \times 10^4 \text{sq cm/gm}$$

If, however, the analysis were stopped at 0.001 mm the contribution would be:

$$S_2 = 0.02264 \left(\frac{58.8-57.8}{0.001/10} + \frac{57.8}{1/2 \times .001/10}\right) = 2.63 \times 10^4 \text{sq cm/gm}$$

Similarly, if the analysis is stopped at 0.00063 mm and 0.00004 mm, the contributions are S_3 and S_4, respectively:

$$S_3 = 4.04 \times 10^4 \text{sq cm/gm}$$
$$S_4 = 31.8 \times 10^4 \text{sq cm/gm}$$

It appears, therefore, that specific surface must be defined with reference to the lower limit of analysis, and that its utility as an index of physical and chemical properties of the soil depends on the relation between the lower limit and the property it is proposed to study.

The lower limit of analysis has been 0.00004 mm, i.e., $10^{-5.4}$ cm in all calculations for specific surface included in this chapter.

Graphical Method of Calculating Specific Surface of Soils

The graphical method of calculating specific surface has been

previously used by Krauss. This method is mentioned by Robinson. The Krauss method suffers from the disadvantage that he uses the idea of settling velocity. The velocity, being dependent upon the temperature at which the sample is analyzed, will not be constant for experiments performed at different temperatures.

The method now developed is based on the idea that if a quantity y is plotted against a quantity x, the area enclosed between the curve and the axis of x and any two ordinates, y_1 and y_2 is given by the integral of y with regard to x between the limits y_1 and y_2. When the quantity does not vary by infinitesimal steps, but takes on discrete values, this integral reduces to the summation, $\Sigma y . dx$ taken between the limits y_1 and y_2.

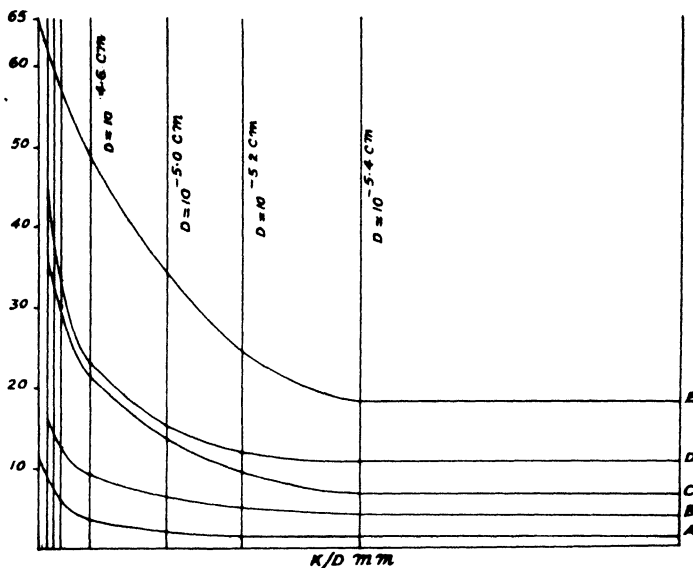



Fig. 26. Graphical Method of Calculating Specific Surface

The expression for the specific surface can be written as $\Sigma K \frac{dP}{D}$ where P is the percentage of particles having a diameter lower than D, and K is a constant independent of size (and is equal to 0.02264).

Consequently, if we plot P against $1/D$ the area of the resulting curve enclosed between the $1/D$ axis and the ordinates at the points $1/D_1$ and $1/D_2$ will equal 1/K times the specific surface. If we further choose the scale along the $1/D$ axis in such a manner that the constant K is absorbed, it will be possible to get the value of the specific surface by a direct reading of the area by means of a planimeter.

The smallest size is limited by the degree of refinement to which the analysis can be pushed. In the present case the smallest size is $10^{-5.4}$ cm. All the particles below this size, as mentioned above,

are treated as if they had a mean size equal to half this size. The curve has therefore been horizontally extended for a distance proportional to $2/D$, where D is the smallest size.

The method is explained by reference to Figure 26. The sizes for which the percentage determinations are made are $10^{-5.4}$, $10^{-5.2}$, $10^{-5.0}$, $10^{-4.6}$, $10^{-4.2}$, 10^{-4}, $10^{-3.6}$, $10^{-3.2}$, 10^{-3} cm. Particles larger than 10^{-3} cm did not contribute appreciably to spe-

Table 34. Comparison of values of specific surface determined by various methods.

Specific surface determined by various methods.

Soil No.	Direct Calculations	Graphical method	Calculated from percentage of particles below .00004 mm.
	x 10^4	x 10^4	v 10^4
A.	1.66	1.56	1.49
B.	5.63	5.77	5.55
C.	10.57	11.12	9.80
D.	14.69	14.66	14.20
E.	27.46	27.58	24.90
2.	37.36	37.58	37.74
3.	45.74	46.65	48.71
4.	4.40	4.60	4.52
5.	4.12	4.44	4.52
8.	22.08	22.90	25.06
9.	12.28	12.66	11.78
10.	27.84	28.12	28.04
11.	25.80	26.66	28.40
12.	5.52	5.68	6.14
13.	37.26	38.41	37.70
14.	20.80	20.96	20.24
15.	8.68	8.66	7.96
16.	2.36	2.48	2.91
17.	7.52	7.17	7.34
19.	23.00	22.47	21.81
20.	3.88	3.65	4.79
21.	5.25	5.72	5.60
22.	5.84	5.82	6.01
23.	3.28	3.84	5.47
24.	6.68	6.82	7.36
25.	1.52	1.56	2.22
27.	3.72	3.53	3.59
29.	31.32	31.62	30.20
36.	3.30	3.36	3.44

cific surface and have been neglected. The process will be clear by reference to Figure 26 in which the curves have been drawn for five of the soils.

The horizontal axis shows the summation percentages. The ordinate marked (K/D mm) is for the smallest size obtained in the analysis, and the ordinates to the left of it represent the gradually increasing sizes.

Comparison of the values of specific surface for these five soils, as well as for a number of others, as obtained by calculation and as given by the planimeter quadrature is shown in Table 34.

The agreement within the limits of experimental error appears to be fairly close. The plotting and the reading of the curve by planimeter takes only about five minutes while the calculations usually take 30 to 40 minutes.

Specific Surface as Determined from Percentages of Clay and Ultra-Clay Particles

It is of interest to study the relation of specific surface to the percentages of fine fractions such as those represented by 0.002, 0.001, 0.00063 and 0.00004 mm limiting diameter. The last two sizes were classed as "ultra-clay" and 0.00004 mm represented the lower limit of analysis for which the specific surface was calculated.

The object of studying the values of the specific surface in relation to percentages of particles below various limits was also to establish the size to which the analysis should proceed in order to make a reasonable estimate of the specific surface. Thus if the specific surface up to 0.00004 mm could be correctly estimated from the clay percentage below 0.002 mm it would not be necessary to analyze down to 0.00004 mm to evaluate the specific surface. The results of the correlations are given below. Ninety-five sets of values were included in these correlations.

1. Correlation coefficient

between SS and P_1 $(<0.002 \text{ mm}) = 0.7926 = r_1$

P_2 $(<0.001 \text{ mm}) = 0.8522 = r_2$

P_3 $(<0.00063 \text{ mm}) = 0.8788 = r_3$

P_4 $(<0.00004 \text{ mm}) = 0.9728 = r_4$

2. Formulae:

(i)....... $SS = (3.36P_1 + 0.37) \times 10^3$

(ii)...... $SS = (3.89P_2 + 0.71) \times 10^3$

(iii)..... $SS = (4.30P_3 + 1.57) \times 10^3$

(iv)..... $SS = (13.51P_4 + 17.37) \times 10^3$

The following conclusions may be drawn from these correlations. The reliability of estimation increases as the percentage of particles of decreasing sizes in the region of ultra-clay are considered.

It is found by testing the differences between r_1 and r_2 and r_3 that they are not significant, but that r_4 is significantly greater than all of them. It appears that in estimating SS it is necessary to go down to the least size included in SS calculations in order to get the best estimate. This is because the smallest sizes are usually the biggest contributors to the value of SS.

If the ultra-clay percentage below 0.00004 mm (P_4) is known, then the specific surface can be estimated from the relation

$$SS = (13.51_4 + 17.4) \times 10^3$$

This relation affords a convenient method of estimating the specific surface of soils. The values of specific surface of a number of soils as determined by this method are included in Table 34. The agreement between the values obtained by the three methods is fairly close.

It will also be seen from Table 34 that the values of specific surface for some of the soils are of a much higher order than those obtained by other workers for similar soils. This is evidently due to the fact that mechanical analysis in the present case has been pushed to much lower limits of particle size.

CHAPTER XV

PHYSICAL CHARACTERISTICS OF SOILS RELATED TO MECHANICAL ANALYSIS

A knowledge of the physical characteristics of soils is essential from the point of view of soil mechanics. Road engineers have developed for some of the more important physical properties a number of tests such as plastic limit, sticky limit, shrinkage limit, plasticity, index, etc. These tests, though helpful in the quasi-scientific technique of the practical workers, are hardly suited to the advancement of fundamental knowledge.

Of all the physical characteristics of soils associated with their mechanical composition those related to cohesion and resistance to impact appear to be of major importance. A study of these has thrown considerable light on the influence of various factors on the physical properties of soil.

Measurement of Cohesion

Cohesion is the resistance offered by the soil to any force tending to break it. It is generally measured by applying an increasing force on a rectangular or cylindrical block of soil until it breaks. The disrupting stress is applied by a wedge which is forced in by the help of suitable weights. Alternatively, a direct pull is applied to a molded rod of the soil until it breaks.

The difficulty in measuring cohesion in dry conglomerates is due to the unavoidable irregularities inherent in soil make-up and a lack of control of conditions affecting this property. In fact, the results obtained are usually of comparative value only. There is something inherently defective in measuring modulus of rupture by forcing a wedge into a dry prism of soil, and reproducible results can only be obtained under strictly controlled conditions.

The apparatus used for cohesion testing has certain unusual features and has given uniformly consistent and reproducible results. It consists of a spring balance (a personal weighing machine is very suitable) mounted in a framework. The latter carries a threaded rod that can be moved up or down by turning a wheel. To the lower end of this rod is attached an iron cylindrical piece with a 1-inch steel ball fastened to it. The ball has a hollow coupling so that it can be made to press against the test piece without rotating when the threaded rod is brought down by turning the wheel.

An important part of the equipment is the brass mold which gives a semi-spherical pellet of soil of 1 inch diameter. It consists of two pieces which, when put together, exactly fit each other to give a round cavity of 1 inch in diameter and half an inch deep. The soil under test is moistened with water to the sticky point and filled in the cavity, the edges being smoothed with a moistened finger tip. The mold is then split by pulling one portion vertically downward. This is important because a perfect mold is not obtained if the pulling is done sideways, or with a twisting motion. Once the technique is mastered, soil pellets can be turned out by the dozens in a short time. The soil pellets are air-dried and tested by placing under the threaded rod with the flat side downward. When the wheel is turned the steel ball presses against the pellet with increasing force (indicated on the spring balance) until it breaks. There is a slight movement of the spring balance needle backward when this occurs, but there is no difficulty in locating the exact weight at which the piece breaks. A dozen pellets are generally tested for each soil and the mean value taken. A great feature of the method is the small quantity of soil required for the test and the uniformity of the stresses and strains involved.

<u>Measurement of Impact Resistance</u>

Resistance to impact can be measured by finding the Brinell hardness number, which is well known as a standard test for metals, especially steel. A hardened steel ball is pressed into the plane surface of the test piece by means of a "ball pressure press". The load is measured and removed, and the diameter of the circular impression determined with the help of a microscope or pocket lens. If D is the diameter of the steel ball and d the measured diameter of the circular imprint, and h the vertical distance through which the steel ball had sunk, the area of the curved pressed surface is:

$$A = Dh = 1/2\pi D(D - \sqrt{D^2 - d^2})$$

Then if W is the applied load, we have

$$H_b = W/A$$

H_b is called the Brinell hardness number and is usually expressed in kilos per square millimeter. Some numerical values for Brinell hardness number, H_b, may be given by way of illustration and for comparison with soils.

	kg/mm2
Vulcanized fiber	7-16
Zinc	50
Copper	60
Steel	150-300
Soil	0.3 - 3.0

The same apparatus is used as for soil cohesion, with the modification that the lower wheel is marked into 200 divisions. There is also an upright brass piece which indicates the complete turns of the wheel; thus any fraction of a turn can be indicated. The soil under test is brought to the sticky point and filled in a brass ring 1 to 8 cm long and 3 to 5 cm in diameter and allowed to dry. The soil block, on drying, falls out on account of shrinkage. It is then tightly held in a special clamp used for fixing rubber hose onto the iron pipes in automobiles.

The steel ball, which has a diameter of 8 millimeters, is soldered onto an iron rod which can be attached to the lower end of the screw in the cohesion apparatus, in such a way that when the wheel is rotated the ball moves downward but does not turn.

The zero reading of the instrument is taken by pressing the steel ball against the spring balance and giving one complete turn to the wheel. This moves the ball by 4 to 8 millimeters (this will vary according to the pitch of the screw) and the spring balance indicates a certain weight (31.5 kilograms in this case). The clamped soil block is then placed on the balance after releasing the pressure, the steel ball brought against it, and the wheel again given one turn. A portion of the steel ball sinks into the soil and the spring balance records a smaller weight. The wheel is then gradually rotated further until the spring balance records the same weight as it did without the soil block. This extra turn represents the distance (h) through which the steel ball has sunk into the soil block. Since one full turn indicates a distance of 4 to 8 millimeters, the depth of the depression could be measured directly with an accuracy of approximately one-fiftieth of a millimeter. This accuracy could be easily doubled, but this is not necessary for soil work.

We have seen that the Brinell number H_b equals W/A. As W is constant in all tests and A is equal to D_h when D is the diameter of the steel ball and h is the depth of the depression (given by the extra turn) we have

$$H_b = W/D \times 1/h = k/h$$

K is determined once for all for a particular instrument and H_b values are obtained by simply dividing a constant factor by h. The value of K for the instrument used was 1.21.

To illustrate the use of the apparatus and to show the relationship between various measurements, the cohesion values and the Brinell numbers of 18 soils were determined. The influence of clay is illustrated by the following correlation coefficients between the various measurements.

Clay per cent and cohesion values...............0.97
Clay per cent and Brinell numbers..............0.90
Cohesion values and Brinell numbers..........0.90

The cohesion testing apparatus having given uniformly consistent results, it was adopted for studying the influence of various factors on this property.

Influence of Clay

Clay is the most important constituent of soils, for it acts as the binder and is almost entirely responsible for the cohesion in dry soils. The magnitude of the force of cohesion must depend on the points of contact between the particles. Obviously, the smaller the particles, the more numerous are the points of contact in a given weight of the most closely packed soil. This pertains, of course,

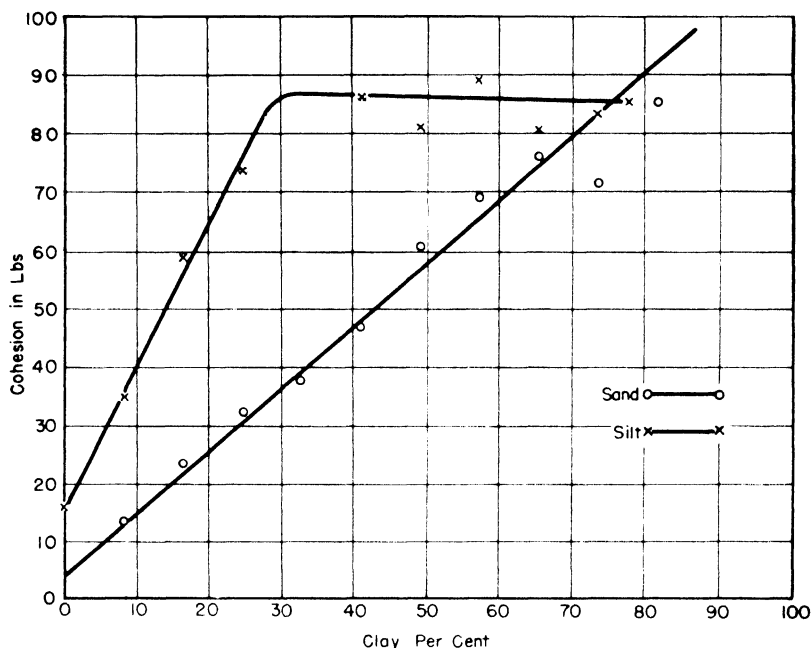



Fig. 27. Relation between Cohesion and Clay in Silt and Sand

only to spherical particles, but the argument will not be materially affected in the case of sand particles of irregular shape for purposes of comparison. Clay acts like glue in binding the particles together, and this cementing action is influenced by the size of the particles.

The effect of increasing amounts of clay on the cohesion in silt (average diameter 0.0764 mm) and sand (average diameter 0.2587 mm) was studied (Figure 27). It will be seen that the cementing action for a given percentage of clay is greater in silt than in sand, though the maximum value is the same in both cases. Another point worth noting is that beyond a certain limit, further additions of clay do not increase cohesion. This condition is evidently reached when all the spaces between the larger particles have been filled with clay, so that any further increase merely pushes these particles

apart, in which case we are, in fact, dealing with cohesion between clay particles which have completely enveloped the larger particles. It is obvious from these results that a much larger amount of clay binder will be required for sand than for silt to attain maximum strength. Therefore, to save as much of the valuable binder material as possible, the voids between the larger particles must be filled with smaller particles of a gradually diminishing size which incidentally is the basic principle of soil grading.

To obtain fuller information on the exact relation between the size of particles and changes in cohesion due to the addition of clay, sand and silt, particles of various sizes were separated by means of the

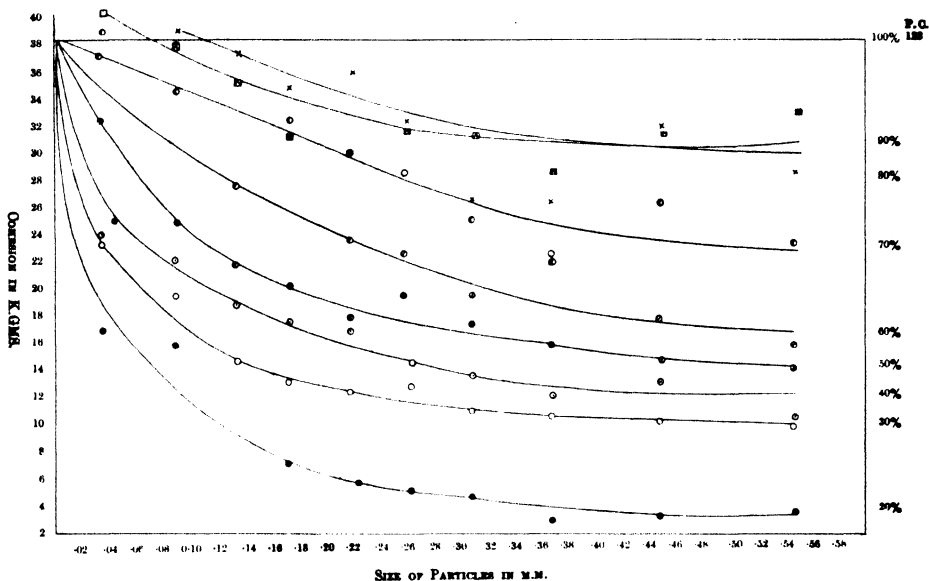



Fig. 28. Effect of Size and Percentage of Particles (Sand) on Cohesion of Clay Soil

Puri siltometer and beaker sedimentation, respectively. Increasing amounts of clay were added to the various fractions and cohesion was measured. The clay was from an alluvial deposit containing 89% of particles below 0.002 mm diameter, and only 5% above 0.02 mm. It was not considered necessary to separate the conventional clay fraction, and all of it was taken as clay for purposes of comparison. The results (Figure 28) show that cohesion for the same percentage of clay rapidly falls as the particle size increases to a limit, beyond which the effect of particle size becomes negligible.

Another interesting point brought out in these results is that the maximum cohesion of 100% clay is of the order of 38 kg. This value is by no means the maximum for clays of different types. In fact, many soils containing much less clay show higher values. It is for this reason that the relation between clay and cohesion in natural soils is only qualitative.

Effect of Hygroscopic Moisture and Nature of Saloid

The effect of moisture on soil cohesion has been studied chiefly in the wetter regions, where it is entirely accounted for by the surface tension of the liquid films of decreasing thickness which draws the particles closer and closer. In the regions of hygroscopic moisture, drying or wetting leads to very little change in volume of the soil as a whole, and consequently the limit of compactness has been reached and the particles can draw no closer together on further drying. This region, therefore, seems to have presented no point of interest, and information regarding it is confined to a few

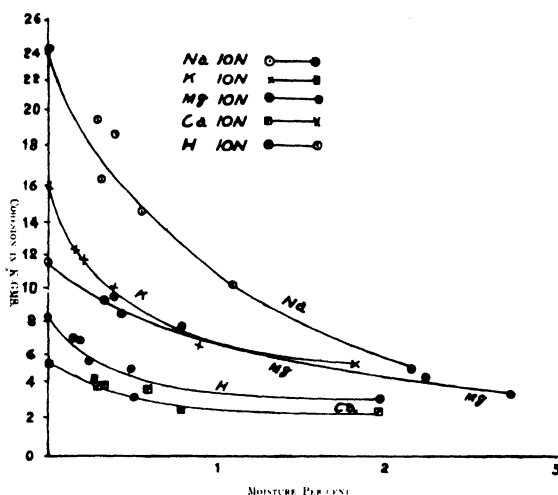



Fig. 29. Effect of Moisture on Cohesion in Various Single-Base Soils

isolated observations. The enormous change in cohesion due to the drying of the hygroscopic moisture leads to the conclusion that beyond a certain degree of wetness the cohesive forces in soils are partly molecular, and therefore may be associated with the nature of the saloids in the clay complex.

The influence of the nature of the cations in soil saloids, as well as hygroscopic moisture was studied on single-base soils by first removing all the exchangeable bases by 0.05N HCl treatment and then adding hydroxides of various metals. The soils were oven-dried and then gradually allowed to take up moisture from atmospheres of different humidities in vacuum desiccators for 72 hours. In the soils to which NaOH and $Ca(OH)_2$ had been added, the relation between moisture and cohesion was also studied by gradually drying the soils. The results are plotted in Figure 29, from which the following conclusion may be drawn.

(1) The effect of the nature of the cations on soil cohesion is maximum when the soil is dry. The absorption of moisture leads to a narrowing of the differences due to ions, which become negligible when the soil is in equilibrium with 90% relative humidity.

(2) The order of cohesion for the dry soil follows the generally accepted order of dissociation for these ions.

(3) The relation between moisture content and cohesion is substantially the same, whether the soil is gradually dried or rewetted.

(4) The greater cohesion in Na and Li soils in comparison with other single-base soils may be due to a stronger bond between the dissociated ions, or it may be caused by the enhanced dispersion of the clay particles. For instance, as shown before, in Na and Li soils, the dispersion of clay is much greater than in the case of other ions. The high dispersion would result in a larger number of points of contact, and the cohesive forces would be greater. The latter view is probably the correct one, for if the soil is first completely dispersed and then converted into a H soil by acid treatment and different ions are introduced as hydroxides without allowing the soil to dry, the cohesion is enormously increased over that of undispersed soil. This will be seen from Table 35, in which the effect of exchangeable ions on dispersed and undispersed soils is compared. The cohesion was measured on the dry soils.

Table 35. Cohesion of soil as affected by various ions, by dispersion, and by remaking of broken pellets

Ions	Undispersed soil		Dispersed soil	
	Original pellet kgm.	Remade pellet kgm.	Original pellet kgm.	Remade pellet kgm.
Li	32.3	40.1	44.5	54.6
Na	23.2	23.2	40.9	46.3
K	16.7	19.1	33.8	29.3
Mg	16.0	15.2	33.1	32.8
Ca	14.1	11.4	27.8	31.2
Sr	10.9	12.9	30.0	29.1
Ba	9.1	12.8	25.9	26.6
H	9.0	......	23.2	21.1

The effect of cations even in the dispersed soils persists. This would seem to indicate that apart from the state of dispersion the cations may have a specific effect. It was noticed, however, in the study of the ultramechanical analysis of soils that although the amount of conventional clay in a dispersed soil was the same whatever the nature of the cation introduced, this was not true of particles finer than clay, which showed a higher percentage in the case of Li and Na ions. These finer particles would easily account for the greater cohesion in Na and Li soils.

The effect of pH value on the cohesion of single-base soils was next studied by adding increasing amounts of the various hydroxides to a H soil (Figure 30). The high cohesion of Na and Li soils is again brought out. It is seen that in the case of Na and K the cohesion reaches a maximum value, beyond which further additions of alkali result in lowering of the cohesion. Li ions, on the other hand, show no such falling off in cohesion. The difference is most probably due to the flocculating effect of NaOH and KOH, an effect which

is absent in the case of LiOH. It might be mentioned that floccula-
tion at these concentrations of NaOH has not been observed in sus-
pensions; but at low moisture contents at which the cohesive forces
come into play, the concentration of the Na ions might easily go
high enough to cause flocculation.

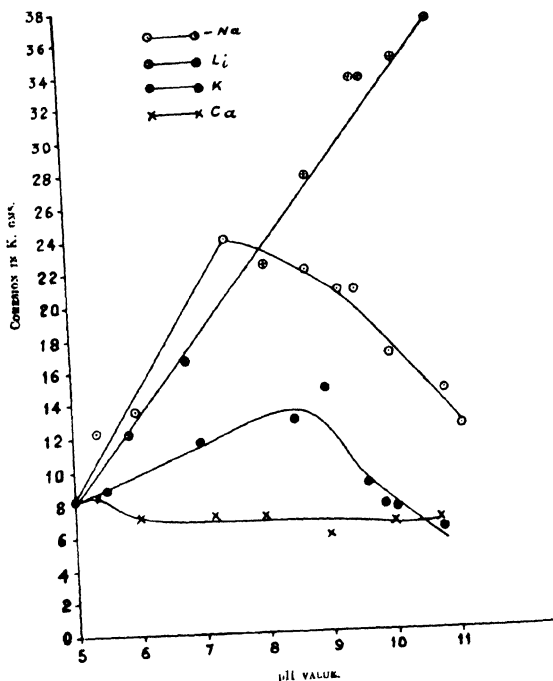



Fig. 30. Effect of pH Value on Cohesion of Soil with Various Ions

Table 36. Effect of $CaCl_2$ on the cohesion of sodium soil

$CaCl_2$ per 100 gm. soil m.e.	Cohesion kgm.
0	32.0
2	26.4
4	24.5
6	24.5
8	20.7
10	19.0

The effect of flocculation with $CaCl_2$ on cohesion of a Na soil was also studied. The soil was first completely dispersed by shaking with Na_2CO_3-NaOH, and then increasing amounts of $CaCl_2$ were added to the suspension until flocculation was observed. It must be understood that the flocculation value of the suspension may not correspond to that of the soil at low moisture content. The decrease in cohesion, therefore, could be expected to have occurred before flocculation was observed, when 8 m.e. of $CaCl_2$ was added. The

results given in Table 36 show that the presence of $CaCl_2$ causes a substantial reduction in the cohesion of the dry soil.

The effect of calcium silicate on the cohesion of the soil must be distinguished from that of other salts. In this case the effect is negligible up to 3% and then becomes pronounced (Table 37). Very likely the enhanced cohesion results from the slow formation of calcium silicate, in which case we are not dealing with the cohesion of the soil but with that of crystals of calcium silicate.

Table 37. Effect of freshly precipitated silicate on soil cohesion

Calcium silicate per cent	Cohesion kgm.
0	16.8
1	15.4
2	17.3
3	17.7
4	32.0
5	44.6

Table 38. Effect on cohesion of heating soils at different temperatures

Nature of Cation	Cohesion kgm.						
	H_2SO_4 dried	150°C.	300°C.	500°C.	600°C.	700°C.	800°C.
Na	24.2	14.0	11.8	14.6	19.1	19.1	24.0
K	16.0	10.0	7.4	8.2	9.6	9.6	13.0
Mg	11.6	6.4	4.1	5.4	6.0	6.0	10.0
Ca	8.2	5.0	3.6	4.1	5.0	5.0	7.3
H	5.4	4.0	3.2	3.2	3.7	4.1	5.4

Table 39. Effect of molasses on the cohesion of Na- and Ca-soils.

	Cohesion kgm.			
Molasses per cent →	0	1	2	3
Na-Soil	23.6	28.0	43.2	41.5
Ca-Soil	10.0	12.3	21.0	20.4

The effect of driving off the water of constitution on the cohesion of soils was also studied by heating single-base soils to various temperatures for four hours. The results (Table 38) show that cohesion first decreases and then increases. The decrease is very likely due to the destruction of the colloidal surface, resulting in a certain amount of contraction and reduction in the points of contact. The initial dehydration is followed by the fusion of the silicates, resulting in an increase in cohesion. It is a remarkable fact that the cohesion of the dry soil is as great as that of the same soil ignited at 800° C.

In view of the importance of molasses in the stabilization of dirt roads, its effect on cohesion was studied in some detail. Increasing quantities of molasses were added to a Na and a Ca soil and cohesion was measured after drying over H_2SO_4. The results (Table 39)

show that both soils give increased cohesion with molasses. The maximum value is reached with 2% of molasses, and further increase apparently has no effect. The high cohesion values for the Na soil as compared to the Ca soil are noteworthy.

To determine whether the enhanced cohesion of the dry soil is lost on rewetting, the Na and Ca soils containing 2% of molasses were rewetted in atmospheres of increasing humidities and the cohesion was determined after the pellets had reached a state of equilibrium with moisture. The results (Table 40) show that cohesion decreases on rewetting.

To explain the binding forces between clay particles in a soil crumb, Russell has put forward the hypothesis that the particles are held together by oriented molecules of a polar liquid. These polar molecules are supposed to lie between negative charges on the clay surface and the exchangeable cations that have dissociated from it, and are strongly orientated in the electrostatic field between these charges. The following objections to this hypothesis may be raised.

Table 40. Decrease in cohesion on rewetting of soil containing 2 per cent molasses

	Cohesion					
Humidity per cent	0	10	30	50	70	98
Na-soil	38.6	38.0	28.2	25.4	16.4	6.4
Ca-soil	25.4	23.0	20.0	18.2	11.8	6.4
Na-soil with cement	18.2	25.4	16.3	14.5	12.3	6.0

Soft crumbs are given only by those liquids in which soil will not disperse, and without dispersion the colloidal clay which acts as binder cannot be released. For the forces of cohesion to come into play, the substance should be either in solution or in a fine state of subdivision in such a way that the residue left on evaporation is amorphous. It is for this reason that gum or glue behaves as an excellent binder. None of these substances would show any binding property if the liquid used did not act as a solvent or a dispersion medium. The important consideration is whether a substance can dissolve or disperse in a liquid and not whether the latter is polar or nonpolar. Certain resins dissolved in nonpolar liquids yield excellent binding material on drying.

If the soil is completely dried, the binding link due to the oriented molecules of the dispersion medium must break down and the soil fall to a powder; but this does not happen. The soil colloids behave like weak electrolytes, and the proportion of cations dissociated is very small compared to the total base (hardly 1%). Any effect due to the orientation of dissociated ions, therefore, would be slight. Further, in accordance with the general behavior of weak electrolytes, the number of dissociated ions must decrease as water evaporates and the solution becomes more concentrated. The loss of moisture therefore must result in a decrease of cohesion--a conclusion contrary to fact.

In view of the enormous increase in cohesion when the last traces of water are removed from soil, any explanation based on the orien-

tation of water molecules is untenable. Not only is the actual amount of dissociated ions in a soil small, but in the presence of even a small quantity of an electrolyte it becomes almost negligible--an amount which would produce no effect on cohesion. It would be a mistake to consider the soil surface as consisting only of dissociated ions. The titration curves of soil suspensions, the changes in conductivity due to dilution, and the rapidity of base-exchange reactions, all point to the fact that the system soil-water is like a homogeneous solution--homogeneous in the sense that the water phase under equilibrium conditions has the same concentration of dissolved cations throughout its entire mass, and in a given system a definite proportion of the cations is dissociated in accordance with the law of mass action.

Table 41. Effect of colloidal substances on cohesion of soil

Rice starch		Skim milk		Egg albumen		Gum arabic	
Amount per cent	Cohesion kgm.	Amount per 100 gm. soil cc.	Cohesion kgm.	Amount per cent	Cohesion kgm.	Amount per cent	Cohesion kgm.
0	21.1	0	21.1	0	21.1	0	21.1
1	37.0	10	24.5	1	29.3	0.25	48.1
2	51.5	20	23.8	2	40.0	0.5	55.3
3	65.6	30	23.2	3	43.6	0.75	57.7
4	72.4	40	25.4	4	51.0	1.00	69.5
5	76.0	50	25.9	5	50.0	1.50	69.5

The exact mechanism of the enormous increase in cohesive forces in soils on drying can be visualized by supposing that the minute interstices between the particles are filled not with water but with a suspension of colloidal clay, which binds the particles together on drying very much like a solution of gum. It will be shown later that the relation between moisture content and relative humidity can be accounted for by the supposition that, as the soil dries, the interstices between the larger particles are emptied and the moisture gradually recedes into the interstices between smaller and smaller particles. The enormous increase in cohesion when the last traces of water are removed is easily understood.

If we accept the hypothesis that colloidal clay acts like glue in binding the larger particles, it would follow that other colloidal substances like egg albumen, gum, rice starch and even skim milk would enhance soil cohesion. The action of substances like sugar and molasses that leave an amorphous residue can also be visualized on a similar basis. In Table 41 are recorded the cohesion values of a soil to which increasing amounts of colloidal substances have been added. The cohesion is more than doubled in the presence of 5% egg albumen and more than trebled in the presence of a like percentage of rice starch or 1% of gum. The effect of skim milk is not so pronounced.

Reversibility of Cohesion

A problem of great practical importance is the reversibility of cohesion. As regards the relation between cohesion and hygroscop-

ic moisture, the reversibility appears obvious. Beyond the slight hysteresis effect, the cohesion increases on drying and decreases on wetting. The point is of considerable importance in water-stabilized dirt roads. The effect of remaking the semi-spherical pellets after breaking them was studied with single-base soils, in both the dispersed and the undispersed state. The results given in Table 35 show that there is virtually no difference in cohesion between the original pellet and the pellet that is powdered and remade into the same shape for test. The difference between the cohesion values for dispersed and undispersed soil has already been referred to, and it is noteworthy that the dispersed soils maintain these higher

Table 42. Cohesion of soil stabilized with molasses, as affected by breaking and remaking, wetting and drying

Original without molasses kgm.	With molasses	
	Breaking & remaking kgm.	Wetting & drying kgm.
21.2	50.0	50.0
	58.2	53.0
	47.0	50.5
	53.6	55.7
	48.2	51.5

values on remaking. It must be emphasized that the nature of the replaceable base is important only indirectly, insofar as it is responsible for determining the state of dispersion of the soil colloids.

Another aspect of the reversibility of soil cohesion which refers to stabilized soils, and which is even more important from the practical point of view, is the question of how far it is possible to restore the cohesion of a soil with water alone after its mechanical breakdown. Obviously substances that are normally insoluble in water and are applied in the form of an emulsion cannot be expected to fall into this category. Soluble substances like molasses, on the other hand, could possibly be brought to the same state of subdivision and intimate mixture with the soil, and the original cohesion restored after a mechanical breakdown. The possibility is not remote, however, that molasses may become oxidized and disappear partly or wholly in the course of time. The irreversibility of soil colloids other than those containing Na saloid would also be an important factor.

Pellets of a soil stabilized with molasses were broken and remade several times, cohesion being recorded each time. It will be seen from Table 42 that the high values of cohesion with molasses are maintained when the pellet is broken and remade. The possibility that repeated alternate wetting and drying might lead to a deterioration of the cohesive bond imparted by molasses was also studied. Soil stabilized with molasses was subjected to alternate drying and wetting by storing over a range of 10 to 90% humidities, cohesion being measured after a definite number of cycles. The results, included in Table 42, indicate that alternate drying and wetting does not alter the cohesive forces.

PART III

SOIL MOISTURE

CHAPTER I

INTRODUCTORY

The majority of investigators of soil moisture concerned themselves with its distribution and movement in the liquid state. Its absorption from the vapor phase received very little attention until much later. Whereas in studies of movement and distribution of water, the total interstitial space is operative, the vapor pressure of soils at different moisture contents is very largely controlled by the minute pores associated with the colloidal portion, and the larger voids have comparatively little influence. For instance, it can be shown that particles of 0.001 mm diameter will have interstitial pores of such dimensions that they will not absorb any moisture from a humid atmosphere unless the relative humidity is as high as 99.5%. It might be pointed out that in soil literature, particles of this size are classed as colloidal clay, which may constitute anything from 5 to 50% of the soil. However, this has so far been considered as the lower limit of particle size in soils and not much attention has been paid to still smaller particles. It is clear that if the conventional clay consisted of particles of 0.001 mm diameter only, moisture absorption from the vapor phase would cease to interest us as far as the soils are concerned. However, the existence of particles smaller than 0.001 mm is proved not only from the fact that soils can absorb moisture from humidities as low as 10%, but by pushing the mechanical analysis to the region of ultra-clay.

The mechanism of moisture absorption by soils and other porous bodies may be explained on the basis of any one of the following current hypotheses:

(1) Capillary condensation: According to this hypothesis the vapors are condensed as bulk liquid in pores as a result of the lowering of vapor pressure brought about by surface-tension effects.

(2) Monomolecular adsorption: The essential feature of this hypothesis is that adsorption takes place by residual chemical valencies and is confined to molecules or atoms that are in actual contact.

(3) Hypothesis of a thick, compressed film: This postulates long-range attractive forces extending out from the surface of a solid. The adsorbed film in immediate contact with the adsorbent

is considered to be under enormous pressure, which decreases as the distance from the surface increases. This hypothesis is not in accord with the current theory of atomic structure and the existence of long-range forces of attraction has not been proved independently in any convincing manner.

(4) Multilayer adsorption: This hypothesis is used to explain the building up of thick films on a plane surface exposed to saturated vapors. If the monomolecular layer is formed by residual valencies of the solid surface, there is nothing to prevent the monomolecular layer already formed from exercising a similar function and attracting another monomolecular layer of the same substance. This process of reasoning could be continued until the actual number of layers found has been reached.

The implications of all these hypotheses have been discussed by McBain, who has rejected the hypothesis of capillary condensation except at high humidities. The main difficulty appears to have been the extremely low values for the diameters of the capillaries required for condensation at low humidities. There is, however, a good deal of misconception as to the mechanism of capillary condensation. For instance, while dealing with sorption by charcoal, McBain has argued as follows: "In the first place the hypothesis of capillary condensation would necessitate the assumption that the pores in the charcoal were all of uniform diameter, that is, equivalent to one long cylinder."

This is typical of the common belief that capillary condensation implies the existence of bundles of tubes in porous bodies. Nothing could be farther from the truth. Not only is such an assumption contrary to the geometry of the primary particle from which all porous bodies must be supposed to have been built, but a bundle of capillaries of uniform diameter would ill accord with the well-established relationship between the relative vapor pressure and moisture content of porous bodies.

On examining moisture and humidity relationships in a vast number of soils we could not help being struck with the remarkable similarity of the isotherms, irrespective of the nature and origin of the soil. This study, when extended to other porous bodies like charcoal and artificial aluminum silicates, brings out the still more remarkable fact that the absorption of vapors by soils and all other porous bodies from atmospheres of different relative vapor pressures can be represented by isotherms which are exactly similar, irrespective of the nature of the absorbent or absorbate. On the face of it any chemical theory would appear out of the question. It certainly could not fit in with any monomolecular layer hypothesis - chemical valence, residual or otherwise.

One of the most serious difficulties in the study of all absorption phenomenon has been the uncertainty about the surface of the adsorbent. There is no way of determining the true specific surface of a body by independent means. The act of adsorption should

not be made use of for calculating the surface, though this has been done with disastrous results.

Soils present a novel method of attack on the general problem of moisture absorption by capillary systems, for they offer an absorbent which admittedly consists of particles of all sizes. The size distribution of the particles can be determined with reasonable accuracy by the methods of mechanical analysis familiar to soil workers. From this, not only can the size distribution of the pores be found, but the total surface can be estimated by assuming a roughly spherical shape for the particles. From the size distribution of the pores the entire relation between relative vapor pressure and moisture content can be theoretically worked out. On the other hand, from the moisture absorption at different humidities the size distribution of the interstitial pores can be calculated, and from the solid geometry of the particles, assuming them to be roughly spherical, the complete mechanical analysis of a soil can be calculated and verified by direct determination by any of the well known methods of mechanical analysis.

Soils are reactive bodies and we have at our disposal some excellent methods of estimating their chemical reactivity, assuming them to be weak electrolytes behaving as weak insoluble acids when freed from bases. Since the chemical reactivity must admittedly be a property of the surface, there are three independent methods of checking up the total surface of soils, namely, direct mechanical analysis, moisture absorption from atmospheres of different humidities, and the chemical equivalence of the acidoid, assuming the surface to behave as such. This method of attack has furnished comprehensive and conclusive proof of the mechanism of moisture absorption as being due to capillary condensation brought about by surface-tension effects.

The subject of adsorption in general is vast and has been dealt with in a number of books on colloidal and surface chemistry. McBain's volume, "The Sorption of Gases and Vapors by Solids" gives a comprehensive survey of the subject and a verdict against the hypothesis of capillary condensation.

In this section we shall deal with one aspect of the subject, namely the absorption of water vapors primarily and vapors of organic liquids incidentally. Facts as discovered are best interpreted by the hypothesis of capillary condensation. The absorption of gases has not been touched. However, the distinction between vapors and gases is not very sharp, and if it could be proved absolutely beyond a shadow of doubt that all moisture down to the last trace is held by the same mechanism, the work on the absorption of gases would be viewed in a new light.

One significant fact might be mentioned in this connection, namely, the sudden increase in the adsorption of a gas when the temperature is lowered below the critical point. In view of the enormous pressures developed in micro-capillaries, the condensa-

tion of the gas to the liquid state is not an impossibility. Another point worthy of note is that the significance of moisture already present in the adsorbent has not been generally realized. In view of the enormous increase of solubility of gases in water under pressure, the possibility of the gas dissolving in the water held in minute capillaries is not at all remote. This aspect of the question has been dealt with in a separate chapter on the absorption of CO_2 by soils at different moisture contents.

One apparently strong argument against capillary condensation is the adsorption on a plane surface, which could be supposed to take place as a monomolecular layer by residual chemical forces. But, strictly speaking, is there such a thing as a plane surface? If we had a microscope that could reveal depressions of molecular dimensions, what a surface we would see! Why not condensation in the space lattice and molecular depressions? The author believes that adsorption from solution has nothing in common with adsorption of vapors and that the two phenomena must be treated quite separately. Attempts to consider them as something similar have led to a vast amount of confusion in dealing with the phenomenon of adsorption in general. This mental attitude is mainly the result of a general similarity of the "adsorption isotherms" in the two cases. In fact, the existence of the adsorption isotherm in every reaction has been considered sufficient evidence in support of the role of adsorption - so much so that admittedly chemical reactions have been ascribed to adsorption. This has not led to any useful generalizations, but has tended to make the confusion worse.

CHAPTER II

SINGLE VALUE CONSTANTS EXPRESSING SOIL MOISTURE RELATIONSHIP

Water being the most important factor for the growth of crops, attempts have been made from early days to find easily determined equilibrium points that would define the property of the soil with respect to its power to hold water. These are described below.

Normal Moisture Capacity

This term was introduced by Shaw. It is defined as the minimum amount of water that is retained by absorption and film forces when water is free to move downward through a mass of uniform soil.

It is determined by packing the slightly moistened soil (first passing it through 1-mm sieve) in a "Pyrex" glass tube 20 inches long and 2 inches in inside diameter. The soil is packed to a depth of 18 inches. The tube is provided with two rubber stoppers having capillary openings, which serve the purpose of equalizing the air pressure and preventing loss of water by evaporation. The soil column is wetted from the top by the addition of distilled water drop wise from a burette, taking care that it is not flooded at any time. The soil surface is covered with a fine screen to prevent puddling. The addition of water is stopped when the soil column has been wetted to a depth of about 15 inches within a week after its addition.

To secure a numerical value for the "normal moisture capacity", the average moisture content of the nearly uniformly wetted portion of the soil column is taken. In obtaining this average, the moisture value for the first one or two inches of the soil is rejected. If a single value is to be taken, the moisture content of the middle portion is quite enough for the purpose. The normal moisture capacity would depend on the method of packing or sampling, on the size and length of the soil columns, and on the time allowed for moisture distribution. It is, therefore, not a fundamental constant for the soil, though it may give a rough indication of the moisture profile in a soil after rain or irrigation.

Field Capacity

Closely allied to normal moisture capacity is the field capacity- the moisture content of a soil, determined usually from 1 to 5 days

after a rain or an application of irrigation water. In sub-humid regions where there is usually a dry layer below the wetted portion of the soil, the moisture conditions are comparable to those required for determining normal moisture capacity. In humid regions naturally the conditions are different.

The Sticky Point

The sticky point is defined as the moisture content of a drying clay paste when it just fails to stick to the fingers or to a nickel spatula drawn across the surface. Keen and Coutts, who made this determination very popular, advocate spreading a wetted 10-gram soil sample on a glass plate with a spatula, and then kneading the sample by hand until the soil no longer sticks to the hands or a spatula drawn through it. There are a number of variations in the technique formulated by individual workers. Whatever sticky point technique is used, it is generally possible to obtain satisfactory duplication of one's own results without difficulty. It is also possible to secure satisfactory checks by those personally instructed by a worker, but not otherwise.

The main difficulty about this determination is the personal factor, which can be eliminated only by some sort of mechanization. Olmstead has described a simple mechanical device for the purpose. It consists of a polished steel roller horizontally held in plain brass bearings, separated far enough for a brass plate to slide between them. The sample under test is mixed with water on the plate and fed against the roller, which is rotated in the direction that forces the soil paste underneath it. The desired end point is attained when the soil barely fails to stick to the roller at a shearing speed of 5 cm per second. The moisture content is then determined by drying at 100 to 110°C. This method appears to offer a more satisfactory basis for a standardized precedure than any of the other methods in use. However, the shearing speed, the size of the roller and the clearance between the roller and the plate must be arbitrarily fixed and specified. The value and use of the information furnished by this determination is not yet certain.

Liquid Limit

The liquid limit is defined as the moisture content at which 10 light shocks produced by striking the dish containing the wet sample against the hand will just close a groove made in the soil. A mechanical method can be used for the purpose. The apparatus consists of a brass dish and cam mounted on a hard rubber block and arranged so that the divided soil cake can be subjected to shocks produced by the fall of the dish through a constant distance and at a specific rate. With this apparatus the number of shocks required to close the groove in the soil at different trial consistencies can be determined. The relation between shocks and moisture content is plotted to form what is known as the flow curve, which is

a straight line on a semilog plot expressed by

$$F = \frac{H - W}{\log M}$$

in which W is the moisture content at M shocks, H is the moisture content at one shock, and F is known as the flow index.

The working conditions are all arbitrarily chosen and must be strictly adhered to for reproducibility.

The Plastic Limit

The plastic limit is defined as the lowest moisture content at which the soil can be rolled into a thread 1/8 inch in diameter, without the thread breaking into pieces.

All published procedures for the determination of the lower plastic limit differ chiefly in the manner of rolling the sample and the end point criterion. The rolling may be done with the fingers, the palm of the hand, or a stick. There is no general agreement as to the diameter or the length of the rolled out filament. No attempt to mechanize the procedure has been made and this constant, though very easy to determine, depends on the judgment of the operator. The test is not applicable to coarse-textured soils and there is no sharp division between soils that have a rolling out limit and those that have not.

The numerical difference between the liquid and the plastic limits, known as the plasticity index, shows the range in moisture contents through which the soil remains plastic.

Minimum Water of Saturation

The minimum water of saturation, also sometimes known as "field moisture equivalent" is the lowest moisture content at which free water appears on the surface of a soil sample in closest packing. It is determined by thoroughly mixing small increments of water with a dried soil and smoothing off with a spatula, until a drop of water placed on the smoothed surface is not immediately absorbed, but instead spreads out and imparts a glisten. After the end point is obtained, the moisture content of the sample is determined in the usual way by drying over-night at 100 to 110°C.

Moisture Equivalent

The equilibrium water content of the soil under free drainage varies so greatly with the manner of packing that it is almost impossible to reproduce field conditions. Briggs and McLane introduced the term "moisture equivalent", which is defined as the percentage of water retained by the soil material under specified conditions in a centrifugal field 1000 times the gravitational field of the earth. This moisture constant is perhaps the best known and most widely used single-value soil property. The main reason for

its popularity is that there is standard equipment available in the market, and if the specified procedure is followed the results can be expected to be reproducible in the hands of different workers.

Olmstead has gone a step further and introduced a centrifugal field of the order of 300,000 times the force of gravity, thus reducing the moisture content to capillaries formed by particles of diameter equal to 0.0001 mm. The application of the principle of removing moisture by centrifuging down to some state of equilibrium is beset with grave difficulties, both practical and theoretical. If the centrifugal force is increased, the soil packing increases simultaneously. It seems unlikely that the packing effect would be a constant factor for all types of soils. A moderate centrifugal force is at least free from such complications. The "moisture equivalent" at 1000g, or centrifugal moisture at 300,000g both represent arbitrarily chosen points on the pressure deficiency (pF)-moisture content curves.

Wilting Coefficient

Wilting coefficient may be defined as the limiting moisture content, below which the plants are unable to draw water for their growth requirements. This may be determined directly by growing plants in a sealed container and withholding moisture from the soil until they show signs of wilting. The moisture content of the soil at the point is determined in the usual way. The main difficulty in this procedure, besides the time required for a single determination, is the observation of permanent wilting, a process which is gradual. Because of the practical importance of this value, attempts have been made to calculate wilting coefficient from some other easily determined equilibrium value. For this purpose the supposed relationship between moisture equivalent and wilting coefficient has found great favor among soil workers. The average value of the ratio between the two as worked out by different investigators, however, is so varied that we are forced to the conclusion that no definite relation exists. Nor is any definite ratio to be expected, since we cannot predict from the moisture content of a soil at one capillary tension what the moisture content will be at another tension. Schofield has made an excellent suggestion in this connection that the wilting coefficient of a soil should be taken when the moisture has receded to capillaries corresponding to pF 4.2.

The three main divisions of soil moisture which have survived until now in soil literature are: (a) gravity water; (b) capillary water; and (c) hygroscopic water.

(a) Gravity water is that water which exists when the soil is flooded and which moves downward when drainage is provided. Of the three forms of water it is the least important. Since the soil can be flooded with any amount of water, it has no fundamental relation to soil structure or other physical constants. We can, therefore, dismiss it as of only historical interest.

(b) Capillary water exists in the pore spaces between the particles, filling them completely or partially.

(c) Hygroscopic water is the water absorbed by the soil from a humid atmosphere. Thus all air-dry soils, not dried artificially by heating, contain hygroscopic water.

In recent years there has been a tendency to abandon the so-called divisions of soil moisture. It is tacitly assumed that all water is held by the same capillary force, the magnitude of which depends on the size of the pores. Hygroscopic and capillary moisture have been dealt with in separate chapters, not because they are fundamentally different, but because they belong to different portions of the range, one pertaining to microcapillaries and the other to macrocapillaries, the same surface-tension effects operating in both cases.

CHAPTER III

CAPILLARY MOISTURE

The simple concept of the soil as a bundle of capillary tubes to which the laws of surface tension and capillarity could be applied was one of the earliest attempts to explain soil moisture distribution. What may, therefore, be called the capillary tube hypothesis found an early place in the literature. Keen, in his review of the subject, has rejected this hypothesis mainly on the ground that experimental evidence in support of it has been lacking. The upward capillary movement in soils is effective only to a limited distance and the lowest of these estimates is in excess of the experimental values with tubes of soils where 4 or 5 feet is seldom reached.

The well known formula for the height to which water rises in a vertical capillary tube which is wetted by water and the lower end of which is in water is

$$h = \frac{4T}{g \sigma d} \qquad \text{(A)}$$

where h is the height of the meniscus above water level, T the surface tension of water in air, g the acceleration of gravity, σ the density of water, and d the diameter of the capillary tube. Substituting the numerical values (C.G.S. system) in equation (A) we have approximately:

$$h = \frac{0.30}{d} \qquad \text{(B)}$$

In applying this equation to the rise of water in soil, d must be regarded as the equivalent diameter of a capillary tube made up of the spaces between the particles. The relation between d and the diameter of the particles D has been worked out by Slichter in the case of an ideal soil, *i.e.*, one having particles of the same diameter. His analysis shows that the value of d at the widest part of the triangular pores between the particles is $0.288D$ where D is the diameter of the spheres in the ideal soil. Equation (B) therefore could be written:

$$h = \frac{0.30}{0.288D} = \frac{1}{D} \text{ (approximately)} \quad \text{(C)}$$

In other words, the capillary pull exerted by a soil column to raise water, or the negative pressure required to pull water from a saturated column, is approximately equal to the reciprocal of the diameter of the particles, both quantities being expressed in centimeters. This extremely simple relationship could be used for

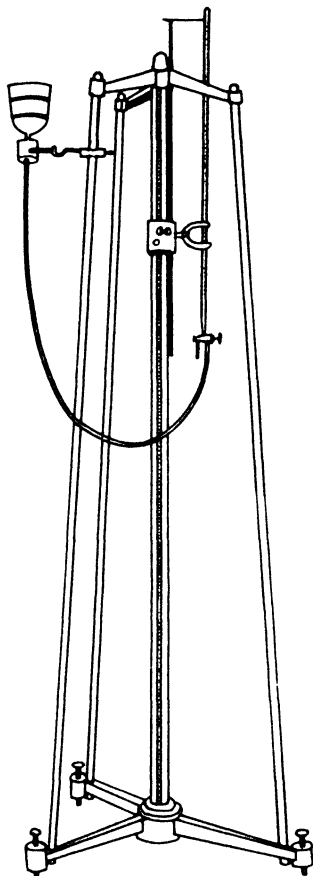



Fig. 1. Diagram of the Capillarimeter

measuring the diameter of particles in the ideal soil or the mean diameter of particles in natural sands and silts. It is necessary only to apply gradually increasing pressure deficiency to a thin column of the particles saturated with water. The point at which the capillary column breaks, would correspond to h, the reciprocal of which would give the mean diameter of the particles.

The apparatus for measuring capillarity, shown in Figure 1, is essentially similar to the one used by Haines, to whose work detailed reference will be made later. The ordinary Buchner funnel used by Haines has been replaced by a sintered glass one, and the

pressure deficiency is applied by sliding a burette tube against a graduated brass cale. There is a rack-and-pinion arrangement worked by a thumb screw which moves a pointer needle against the brass scale as well as the burette scale. The funnel is filled with water by inserting a rubber bung at the top, inverting it, and joining it to the rubber tube leading to the burette. The connecting rubber tube is kept full of water when being joined to the funnel, and if the burette tap is kept slightly open, the flow of water insures an air-free joint. It is essential that no air be allowed to remain at the lower surface of the filtering disc. Excess water is removed from the funnel and is replaced by a quantity of sand to give a layer about 0.5 cm thick with some free water standing on top.

At the start, the level of water on top of the sand and the burette is the same. The burette tube is lowered in steps of 1 cm or so, and the rise of water is noted in terms of the graduation on the tube. As the burette tube is lowered, the pointer needle is raised with the thumb screw, so that any rise of water is compensated, and the reading on the brass scale gives the true value of pressure deficiency to which the sand is subject. Obviously as long as there is free water, there is very little change in the scale reading because of this compensating device. As soon as the free water disappears the tension produced by the lowering of the burette tube is taken up by the surface tension of the water, and any difference in the scale reading from the original value gives the true value of pressure deficiency. From this point onward, further lowering of the burette tube causes no rise in the level of the water contained in it. This constant value continues until the pressure difference exceeds the capillary pull of the sand, and the water again begins to rise in the burette tube. There is a definite break if the layer of sand is only a few millimeters thick, and the value can be reproduced within a centimeter of pressure deficiency. On the other hand, if the sand layer is a few centimeters thick, the capillary front recedes as the burette tube is lowered, and some water is yielded at every step. The sand layer, therefore, must be kept only a few millimeters thick, when a definite break can always be obtained.

It is worthy of note that the sintered glass filtering disc has a capillary pull of its own. If this is greater than that of the sand above, no definite break is observed, in the first instance, because the receding capillaries are held by the filtering disc. The capillary pull of the latter, therefore, should always be lower than that of the sand under examination.

It must be emphasized that there is a limit to the application of pressure deficiency in this particular way, which extends only to the point where the capillaries remain completely full. The moment the continuity of capillary water is broken and air has entered, further application of pressure deficiency by lowering the water

column has no meaning. It is up to this limit that the mean diameter of the capillaries corresponds to the inscribed circle in the triangular space between three spheres touching one another, which is covered by Slichter's mathematical analysis and which alone can be expected to conform to formula (C).

With the help of the capillarimeter described, we can measure the maximum capillary force that can develop in a sand or soil and therefore test the relation between particle diameter and maximum capillary force. For this purpose, 107 sands and 11 soils were examined. Of the sands, 26 were of uniform diameter and had been separated by the siltometer to conform as closely as possible to the diameters given. Others were natural sands obtained from canal beds and were of widely varying origin. The mean diameters were calculated from the relation $h = 1/D$, where h is the maximum capillary pull and D the diameter of the particles. The mean diameters of these sands were also determined from their distribution curves as follows.

The summation curve of a sand or soil sample is plotted on a large-scale graph paper. By taking the readings for two given sizes and subtracting, we obtain the percentage of particles whose diameters lie between the two sizes and which may very nearly be assumed to have a diameter lying midway between them. If this last value is multiplied by the corresponding percentage, and the sum of all such products is divided by the sum of the percentages (usually 100), we get a value for the mean diameter of all the particles contained in the sample. This is the weighted mean size, and incidently furnishes a useful measure of the degree of coarseness of the sample. It will be seen from Table 1A that the agreement between the two sets of values is as good as could be expected, and this leaves no doubt as to the soundness of the capillary hypothesis, especially as the range of diameters studied is from 0.02 to 4 mm. The results with soils need further comment.

The clay content of the soils varied from 11.5 to 68.2%, and the mean diameter refers to their distribution curves obtained at maximum dispersion as well as without dispersion. The maximum capillary force actually determined lies somewhere between the calculated values for mean diameter both at maximum dispersion and without dispersion (Table 1B). This is what one would expect in view of the uncertainty regarding the state of aggregation of a wet soil. It might be noted that particles having diameters of 0.02 cm or more settle quickly to the bottom of the funnel, and the remaining soil behaves as if it were devoid of these particles.

In calculating the mean diameters of the soils, the portion of the distribution curve above 0.02 cm diameter is not taken into consideration, and the results are calculated as if these particles were absent. Another point is that soils should be soaked in water for 24 hours. After this the capillary force is measured as usual. Unlike sands, soils yield some water at every decrease in the vol-

TABLE 1A. Calculated and found values of capillary columns (natural silts).

No.	Mean Diameter	Capillary Columns det'd (cm H_2O)	Capillary Columns calc (cm H_2O)	No.	Mean Diameter	Capillary Columns det'd (cm H_2O)	Capillary Columns calc (cm H_2O)
1	.512	19.8	19.5	42	.181	54.7	55.2
2	.501	20.0	20.0	43	.230	35.6	43.5
3	.493	18.9	20.3	44	.205	49.0	48.8
4	.483	19.8	20.7	45	.189	44.0	52.9
5	.476	21.0	21.0	46	.226	23.5	44.2
6	.467	20.6	21.4	47	.126	83.5	79.4
7	.441	23.4	22.7	48	.129	47.4	77.5
8	.432	22.1	23.1	49	.131	78.0	76.3
9	.403	25.5	24.8	50	.136	67.7	73.5
10	.388	26.8	25.8	51	.151	69.0	66.2
11	.389	28.4	25.7	52	.172	57.2	58.1
12	.345	29.6	29.6	53	.178	59.2	56.2
13	.338	31.6	29.6	54	.208	51.6	48.1
14	.325	33.2	30.8	55	.197	61.7	50.8
15	.320	33.0	31.3	56	.202	46.3	49.5
16	.288	41.3	34.7	57	.159	67.4	62.9
17	.225	40.0	39.2	58	.250	41.0	40.0
18	.381	28.0	26.2	59	.133	79.7	75.2
19	.355	26.5	28.2	60	.204	50.6	49.0
20	.278	36.2	36.0	61	.340	29.3	29.4
21	.274	38.0	36.5	62	.363	30.5	27.5
22	.274	36.0	36.5	63	.369	29.3	27.1
23	.330	32.7	30.3	64	.313	32.2	31.9
24	.353	32.0	28.3	65	.242	44.7	41.3
25	.711	17.5	14.1	66	.205	45.0	48.8
26	.646	21.4	15.5	67	.306	35.7	32.7
27	.636	17.8	15.7	68	.225	42.1	44.4
28	.684	17.6	16.0	69	.227	43.7	44.1
29	.231	44.4	43.3	70	.269	34.0	37.2
30	.332	31.3	30.1	71	.356	27.2	28.1
31	.227	41.4	44.1	72	.215	48.0	46.5
32	.141	66.4	70.9	73	.201	43.5	49.8
33	.117	94.3	85.5	74	.261	40.5	38.3
34	.166	56.9	60.2	75	.245	37.7	40.8
35	.185	55.5	54.1	76	.250	40.8	40.0
36	.188	55.3	53.2	77	.283	35.0	35.3
37	.201	52.5	49.8	78	.351	28.8	28.5
38	.216	46.4	46.3	79	.263	39.0	38.0
39	.179	64.3	55.9	80	.338	28.8	29.6
40	.223	47.1	44.8	81	.332	24.7	30.1
41	.147	42.7	68.0				

TABLE 1B. Calculated and found values of capillary columns (soils).

P.C. Soil No.	Clay (%)	Mean Diameter Dispersed	Mean Diameter Un-dispersed	Capillary Column Det'd (cm Hg)	Capillary Column Calculated Dispersed (cm Hg)	Capillary Column Calculated Undispersed (cm Hg)
1	11.50	.0246	.0373	22.80	30.00	19.79
2	64.06	.0229	.0730	18.8	32.23	10.11
3	68.21	.0233	.0737	21.3	31.67	10.01
4	15.56	.0329	.0499	24.4	22.43	14.79
5	12.79	.0342	.0475	18.5	21.58	18.54
6	29.73	.0326	.0642	19.0	22.64	11.50
8	27.30	.0497	.0789	17.4	14.85	9.35
9	22.90	.0493	.0863	9.0	14.97	8.55
10	38.62	.0394	.0845	21.0	18.73	8.73
11	35.08	.0435	.0980	16.0	16.97	7.53

ume of the soil, as the water is squeezed out and the particles come closer and closer. This phenomenon is entirely due to the swelling of soil colloids and is not fundamentally related to the moisture content and pressure deficiency. Moreover, as equilibrium is reached at a much lower rate in soils than in sands, at least 15 minutes are allowed between successive readings.

TABLE 1C. Calculated and found values of capillary column (silt and sand fractions).

No.	Mean Diameter (mm)	Capillary Column det'd (cm H_2O)	Capillary Column calc (cm H_2O)
1	3.0 - 4.0	3.5	2.9
2	2.0 - 3.0	5.4	4.0
3	1.3 - 2.0	6.3	6.1
4	1.0 - 1.3	8.8	8.7
5	0.88 - 1.0	13.0	10.6
6	0.6	14.0	16.7
7	.56 - .60	23.2	17.24
8	.49 - .56	24.4	19.0
9	.44 - .49	27.4	21.5
10	.40 -- .44	26.6	23.8
11	.36 - .40	29.7	26.3
12	.34 - .36	30.6	28.6
13	.31 - .34	32.8	30.8
14	.29 - .31	36.3	33.3
15	.28 - .29	36.3	35.1
16	.26 - .28	37.8	37.0
17	.25 - .26	36.7	39.2
18	.22 - .25	41.1	42.6
19	.20 - .22	44.9	47.6
20	.19 - .20	46.0	51.3
21	.17 - .19	50.4	55.6
22	.15 - .17	55.9	62.5
23	.13 - .15	69.1	71.4
24	.12 - .13	77.0	80.0
25	.08 - .12	90.6	100.0
26	.065 - .08	94.1	137.9
LEAD SHOTS			
1	1.32 - 1.5	6.8	7.1
2	1.0 - 1.32	7.9	8.6

While studying the capillary force of soils, it is not convenient to work with water columns 3 or 4 meters long. The burette tube and a part of the connecting tube are filled with mercury, therefore, and the pressure deficiency is applied by lowering the mercury column, which can be converted into terms of the height-of-water column if required. In Table 1C the calculated and found

values of capillary pull of soils are given in terms of the mercury column.

It is interesting to note that the maximum height of the capillary column, both calculated and determined, for a soil containing as much as 68% clay is of the order of 10 to 12 feet, and in some cases it is much less. This is the usual height found in normal natural soils. One reason why Keen and several other soil workers have rejected the capillary tube hypothesis of soil moisture is that the theoretical value of upward capillary movement is by no means approached in actual practice.

It is evident that the importance of the mean diameter in calculating the theoretical value has not been realized, and abnormally high calculated values have been assumed. For instance McGee, from his work in the Great Plains of America, concluded that water could rise at least 10 feet in a year, and 30 to 35 feet in a favorable term of years. Hall has given a rise of 200 feet and Mitscherlich calculated a rise of several hundred feet.

Schofield has endeavored to express the moisture content of soils in terms of free energy relationships. If we suppose that water is held by soil against a suction force tending to displace it, the free energy can be expressed in terms of the height in centimeters of the equivalent water column. To deal conveniently with the whole range of suction, use is made of the logarithmic acidity scale. The symbol pF has been used (F being the recognized symbol for free energy). From equation (C) we can express the relation between the diameter D of particles and its pF as:

$$pF = -\log D$$

We can, therefore, express the summation curves of soils in terms of free energy, or pF. Such curves, of course, will not be different from the ordinary summation curves on the semilogarithmic scale, but they will bring out more clearly the fact that in soils we have particles of a diameter which can form capillaries of the order demanded by theory.

Summation values and other relevant data for two soils are given in Table 2. Particles up to the diameters corresponding to pF 5.03 were determined by the pipette method, using the micropipette technique; values for pF 6 were extrapolated from the summation curves. It is admitted that not much reliance can be placed on the extrapolated values on a logarithmic scale, but there is no mistaking the general trend of the extrapolated portion. These soils are of unusual interest, because in spite of the fact that P.C. 123 contains a much higher percentage of conventional clay than does P.C. 13, the former absorbs less moisture at all humidities below 93%, as will be seen from Figure 2. At this humidity, corresponding to pF 5, the curves cross, and at higher humidities P.C. 123 absorbs more moisture than does P.C. 13.

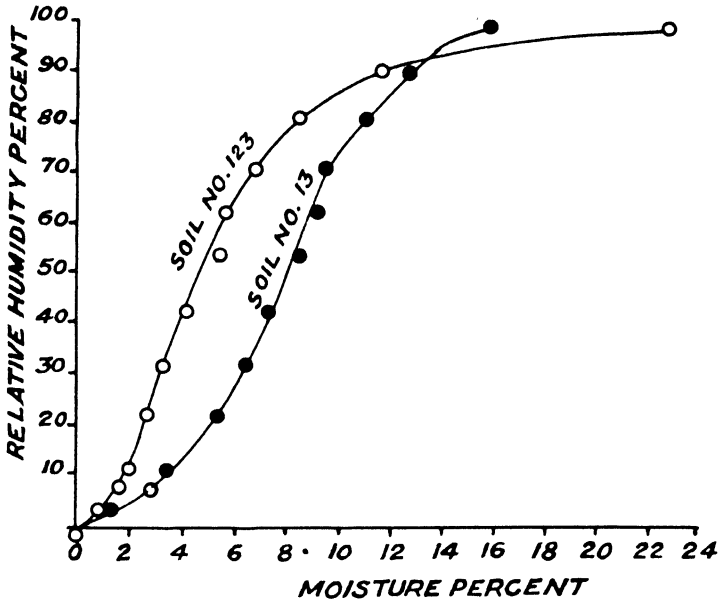



Fig. 2. Relation between Moisture Content and Relative Humidity in Two Soils

TABLE 2. Relation between diameter of particles and their summation percentages for two soils.

Diameter (cm)	pF	Summation percentages P.C. 13	Summation percentages P.C. 123	Relative humidity (%)
.006	2.22	93.4	98.0	--
.004	2.40	89.5	98.1	--
.002	2.70	88.0	97.9	--
.001	3.00	79.0	97.0	--
.0008	3.10	77.0	96.8	--
.0005	3.30	73.0	96.0	--
.0002	3.70	58.8	90.9	--
.0001	4.00	56.9	87.9	99.5*
.000043	4.37	48.6	74.7	97.0
.000023	4.64	46.2	59.0	96.5
.0000016	4.80	45.0	49.8	95
.0000094	5.03	45.7	39.2	92
.0000001	6.00	40.0	12.0	40
.0000001	7.00	--	--	0

*Calculated from the formula:

$$pF = 6.5 \log_{10} (2 - \log_{10} h)$$

where h is relative humidity.

It will be seen that pF 7, which corresponds to the oven-dry state, also marks the lower limit of the colloidal state. Particles of diameter 10^{-7}cm, corresponding to pF 7, will have a capillary diameter of the order of 3 x 10^{-8}cm. In other words, particles of this size will be packed so closely that even a single molecule of water could not be squeezed between them; thus all capillary moisture ceases to exist. It is significant how the colloidal state in soils merges into the molecular state. It is, therefore, not difficult to understand that many of the so-called adsorption phenomena in soils may be essentially of a chemical nature, and in no way different from similar reactions in molecular dispersions (solutions).

The extreme limit of conventional clay, *i.e.*, particles of 0.0001 cm diameter, corresponds to pF 4, which is equivalent to a relative humidity of 99.5%. Particles of larger diameter, therefore, give capillaries that are too coarse to be filled through the vapor phase. This explains the often quoted fallacy that it is not possible to saturate a soil completely from a fully saturated atmosphere. It is also clear that the region of hygroscopicity lies below the particle size of conventional clay, and an explanation of the varying hygroscopicity of clays lies in the size distribution of ultra-clay particles. A semi-quantitative relation between conventional clay and hygroscopicity is also apparent from these considerations. A general similarity in the shape of the mechanical analysis summation curves and relative humidity moisture content curves can also be understood. This similarity would be still more striking if we could compare the ultra-mechanical analysis of particles smaller than conventional clay. This aspect of the question will be examined in greater detail later.

We have seen that a sand consisting of particles of 0.01 cm diameter requires a suction pressure of the order of pF 2 (100 cm) to overcome the surface tension of the water held in the capillaries. We can, therefore, vary the pF from 0 to 2 without altering the moisture content. For a finer sand, say 0.001 cm diameter, the suction force must exceed pF 3 before any water can be drawn out. It is clear, therefore, that there must be an abrupt drop in the pF moisture content curve starting with a saturated sand. In soils, this abrupt drop is masked by secondary effects, and as the pressure deficiency is increased, some water is yielded at every step though the soils remain saturated. Let us try to visualize the cause of this apparent anomaly.

The fact that soils swell on absorbing water is well known, but the mechanism is not quite clear. We are, generally content with the statement that water somehow could make room for itself by separating the particles slightly from one another. The real situation can be very well imagined if we recall the property of "auto-disintegration" by virtue of which soil colloids go into suspension without being shaken. We can imagine the larger interstices between compound particles as being just filled with water. This is

followed by the auto-disintegration of colloidal clay, accompanied by an increase in volume, because the particles that were originally most closely packed are no longer so. In the end the capillaries are filled - not with water, but perhaps with a highly viscous fluid constituting a clay suspension of density greater than water. In an extreme case the larger particles could float in this suspension, and the entire mass would become plastic.

If suction is applied at this stage, water filters out and the volume decreases correspondingly. This continues until the soil aggregates are most closely packed. That this might be a true picture of the swelling of soils is supported by the fact that this phenomenon is most pronounced in Na and Li soils, the colloidal clays of which are known to impart to the soil the property of auto-disintegration. The yield of water from a saturated soil by suction, therefore, is due to the filtration of water from the clay suspension held in the interstices, and the force required is used in overcoming the elastic rigidity of a thick suspension. The relation between pF and moisture content in this region is, therefore, not real, and is influenced by the fact that the interstices may be filled not with water, but with a clay suspension.

The absorption and removal of water from a soil is a slow process, and the attainment of equilibrium may take several days. An interesting experiment may be cited to illustrate this point. If to a saturated sand column held under a pressure deficiency some water is added, all of that water passes on to the burette tube of the capillarimeter. On the other hand, if the experiment is repeated with soil, the water may take several days to pass on to the burette tube, and even then some of it may be retained in the soil. This part goes to swell the soil mass. Similarly, soil may continue to yield water for several days under a certain pressure deficiency. It is for this reason that determination of the true value for the capillary pull of soils is difficult. Even the approximate values leave no doubt, however, that the forces involved are the same, both in sands and in soils.

Since the height of a column of liquid supported by capillaries of a given diameter varies as the surface tension of the liquid and inversely as the capillary diameter, almost any liquid could be used for finding the mean particle diameter. Alternatively, this relation could be used for comparing surface tensions of liquids other than water. For instance, if T_l is the surface tension of a liquid and T_w the surface tension of water, then:

$$T_l = \frac{T_w \cdot H_l}{H_w} \qquad \text{(E)}$$

where H_l and H_w are the heights of the capillary columns for the liquid and water, respectively. Since T_w is constant and H_w can be

kept constant by using particles of the same diameter, (E) can be written:

$$T_l = KH_l \qquad \text{(F)}$$

in which K is a constant characteristic of the grade of sand used.

The surface-tension values of a number of organic liquids were determined by means of formula (F), sand of 0.475 mm mean diameter being used. The results given in Table 3 show good agreement with the standard values from "International Critical Tables". The experiments were extended to the determination of interfacial tensions between water and some organic liquids lighter than water. These liquids were floated on the water. When the free water surface disappeared as a result of the application of pressure deficiency, the interfacial tension came into play. The break point was as definite as that in the water-air interface. Actually no sand was used in this case. The porous plate of the sintered glass funnel was used for applying the capillary tension. A comparison of the interfacial tensions determined in this way and standard values, also given in Table 3, shows good agreement. The liquids chosen were those available in the laboratory, and no special care was taken to insure their purity, as the whole object of this experiment was to illustrate a principle rather than to elaborate a method of measuring surface tensions. There is no doubt, however, that the method is capable of refinement and might be employed with some modification for measuring surface tensions.

TABLE 3. Surface tension and interfacial tension values of liquids determined by the capillarimeter, compared with standard values.

Liquid	Surface tension		Interfacial tension	
	Found	Standard	Found	Standard
Benzene	34.9	28.9	37.8	35.0
Phenetole	32.5	32.7	33.0	29.4
Amylbutyrate	29.4	25.2	18.3	23.0
Hexane	21.8	18.4	48.8	51.1
Ethyl Ether	18.3	17.1	10.3	10.7
Toluene	--		38.1	36.1
Oleic acid	--		18.3	15.6
Xylene	--		41.4	37.8
Isobutylchloride	--		24.2	24.4
Mesitylene	--		33.0	38.7
p-Cyamine	--		31.2	34.6

The fact that almost any liquid could be used for measuring the mean diameter of particles in the capillarimeter is of great importance in studying the crumb structure of soils as it exists in nature, and which is at once altered as soon as they are brought into contact with water. The use of benzene, alcohol or kerosine, for instance, in this case would give a true measure of the particle

sizes as they exist in nature. To illustrate the point under discussion, the mean diameters of a few soils determined in water as well as in benzene, alcohol and kerosine are given in Table 4.

It will be seen that the values of mean diameter in water in all cases are lower than those in alcohol and are the highest in kerosine. This is in agreement with the general observation that water has the greatest disintegrating effect on soil crumbs. The close agreement between the two sets of values leaves no doubt as to the correctness of the capillary hypothesis or the utility of the capillarimeter for measuring mean diameters of soil aggregates in the natural state.

TABLE 4. Mean diameter of soils determined in the capillarimeter and calculated from mechanical analysis in various liquids.

P.C. Soil No.	Mean Diameter (mm)							
	Water		Alcohol		Kerosine Oil		Benzene	
	Mec.An.	Cap.	Mec.An.	Cap.	Mec.An.	Cap.	Mec.An.	Cap.
6	.0642	.061	.1458	.120	.2814	.22	.2052	.181
13	.1420	.118	.306	.330	.359	.368	.344	.354
72	.0124	.0104	.2032	.199	.296	.288	.2476	.263
110	.0624	.046	.1805	.160	.278	.249	.2228	.240
121	.0273	.020	.1941	.265	.265	.249	.199	.214
123	.0062	.0087	.2234	.210	.300	.310	.260	.280

TABLE 5. Mean diameters of cements determined in the capillarimeter and calculated from mechanical analyses in various liquids.

Cement No.	Mean diameter (mm)					
	Kerosine		Benzene		Alcohol	
	Mec. An.	Cap.	Mec. An.	Cap.	Mec. An.	Cap.
I	.0576	.0598	.0482	.0471	.0312	.0310
II	.0618	.0614	.0478	.0458	.0308	.0305
III	.0536	.0576	.0512	.0482	.0299	.0301
IV	.0555	.0576	.048	.0458	.0306	.0303

The application of the same principle in finding mean diameters of cements by using organic liquids is also indicated. Four cements were examined by the capillarimeter using kerosine, benzene and alcohol: they were also mechanically analyzed, using the same liquids for sedimentation. The results given in Table 5 bring out the general agreement between the two sets of values. The lower values in the case of alcohol are also significant.

Hitherto we have discussed only the rupture of the water film in the widest part of the capillary spaces in an assemblage of particles, characterised by the largest inscribed spheres in the triangular spaces between the particles. This, however, is by no means the only moisture held in the interstices; a good deal more

is held in the wedge-shaped corners. To determine the variations of moisture with pressure deficiency in this region the capillary pull of the sintered glass porous plate in the funnel of the capillarimeter must be greater than that of the sand or soil under examination, so that the application of pressure deficiency can be extended beyond the rupture of the main capillaries. This has been done by Haines, who has dealt with the hysteresis effect in capillary properties and the modes of moisture distribution associated therewith.

From a consideration of the solid geometry of the spherical particles and the wedge-shaped water films contained in the interstitial pores, he concluded that water in the soil may be distributed in discrete rings, one around each point of contact between the spheres. This is the "pendular" stage according to Versluy's nomenclature. When the volume of moisture is increased beyond the pendular stage, the water wedges establish contact, and it is possible to pass from any point in the water film to any other without leaving the liquid phase. In Versluy's nomenclature, this is the beginning of the "funicular" state. On further additions of water the saturated zone will progressively extend to the "capillary" stage, when the pores are completely filled with water. The pendular stage can extend from dryness to 24% saturation of the pore space, the pressure deficiency falling meanwhile from a theoretical infinite value to 12.9 x T/r. (T being surface tension and r the radius of the particles). The funicular stage extends beyond 24%. The capillary or saturated stage is completed when 100% of the pore space is occupied by water. The theoretical values for the pressure deficiency associated with different stages of moisture when pressure deficiency is applied to a saturated sample are as follows:

At a pressure deficiency equal to 4.1 T/r penetration of air is first observed. Gradual entry of air takes place at a pressure deficiency of 6.1 T/r, where the capillary stage ends and the funicular stage begins. Thereafter some 70% of the water is lost up to a pressure deficiency of 12.9 T/r. Beyond that stage the general reduction of the funicular water takes place gradually until there is an abrupt cessation of water movement due to the break in film continuity, and the moisture enters the pendular stage. This takes place at a pressure deficiency of 12.9 T/r. The three critical values for pressure deficiency, namely 4.1, 6.1 and 12.9 (T/r) were directly verified by Haines for spheres in closest packing. The outstanding feature of his results is the distinction between the rising and falling moisture curves and the restricted range for reversible conditions. It was also found that there is no unique relation between pressure deficiency and moisture content; by suitable cycles of rising and falling moisture the material can be brought to any stage within the hysteresis loop. Independent experimental confirmation of these values is given by Hackett and Strettan.

As pointed out before, most of the experimental verifications of theoretical considerations have been obtained with the so-called "ideal soils", that is, with particles of uniform diameter. Since the radius of the particles has to be taken into account, the remarkable agreement between the theoretical and experimental values for the maximum pull, in the case of natural silts obtained when "mean diameter" of the particles is taken as the basis of calculations, led to the belief that similar results might be expected in the case of experimental elucidation of the three stages of soil moisture.

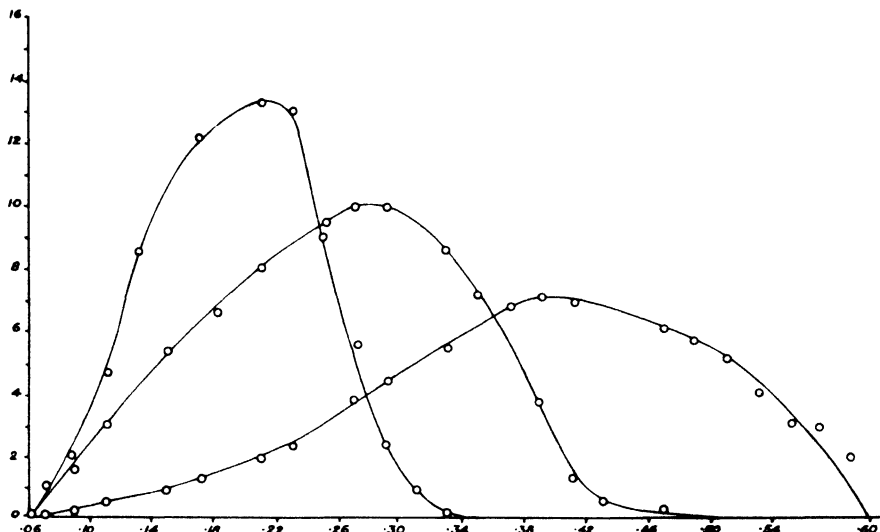



Fig. 3. Examples of Distribution Curves

Particles of uniform diameter were obtained by grading natural sand with the siltometer. This instrument, as described before, consists of a long sedimenting tube, the lower end of which opens into a moving trough with boxes arranged around it. The boxes move in position under water by means of a lever, and thus come under the sedimenting tube one after the other; thus the silt moving in the water column in the tube is graded into 20 fractions, the content of each box representing each size within a narrow range. The size distribution curves of some of these silts are given in Figure 3.

It will be seen that though the bulk of the silt sample consists of particles of the given diameter, they are by no means the only particles present. Incidentally, it might be mentioned that separation of particles of a particular size with the siltometer is only partial, so that if the contents of a particular box corresponding to a definite size are again passed through the siltometer, all the particles will not fall into the same box. The major portion does so, but the remainder is almost uniformly distributed in the ad-

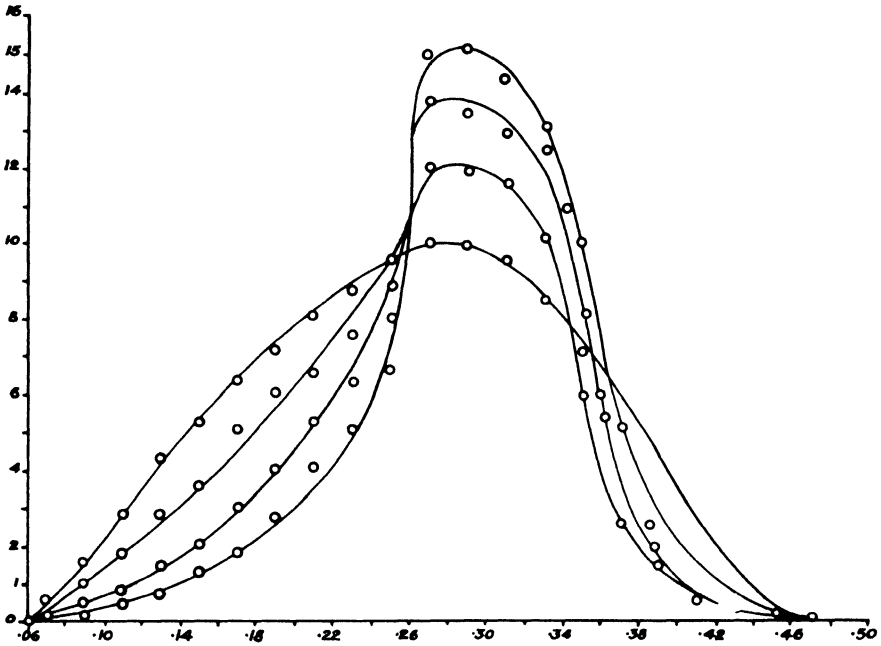



Fig. 4. Distribution Curve as Affected by Repeated Fractionation in Siltometer

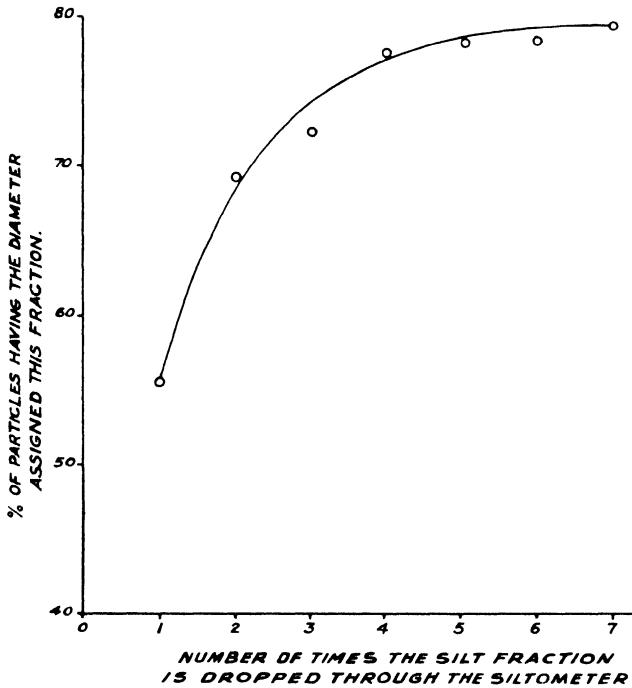



Fig. 5. Fractionation of Silt by Dropping through the Siltometer

joining boxes on both sides of the one receiving the main portion. This will be clear from Figure 4, in which the effect of repeatedly dropping the contents of a particular box through the siltometer is graphically shown. The narrowing down of the maxima in the dis-

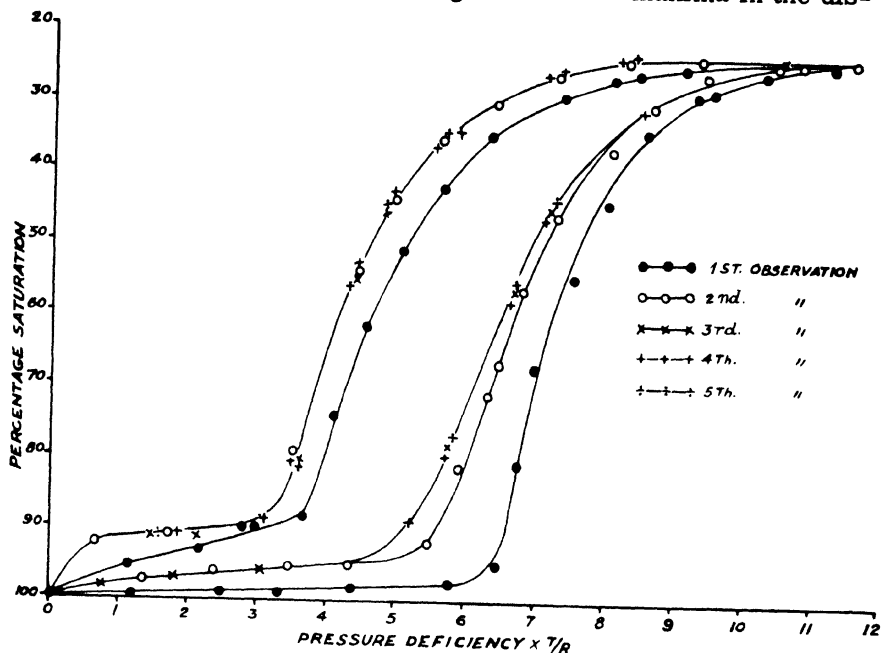



Fig. 6. Pressure Deficiency-Percentage Saturation Curves of a Silt Sample Determined by the Siltometer

tribution curves is clearly indicated. Even after the same sample is passed seven times, the graded sample does not correspond strictly to the diameter corresponding to the particular box. This is brought out still more clearly in Figure 5, in which the percentage of particles having the average diameter are plotted against the number of times the silt sample is put through the siltometer.

Relation Between Pressure Deficiency and Percentage Saturation of Pore Space for Graded Silts

One hundred grams of the silt sample in every case were placed in the sintered glass funnel of the capillarimeter, and pressure deficiency applied by lowering the burette tube gradually, the volume of water yielded at every step being noted. In order to study the reproducibility of results, silt No. 6 of mean diameter 0.28 mm was taken five times through the entire cycle of changes, from the fully saturated state to the pendular stage, and then back to saturation. The results are plotted in Figure 6.

It will be seen that the relation between pressure deficiency and moisture saturation percentage is reproducible, and that the gradual withdrawal of water from the sand and its repeated intake pass through the same sequence of changes. Similar curves were ob-

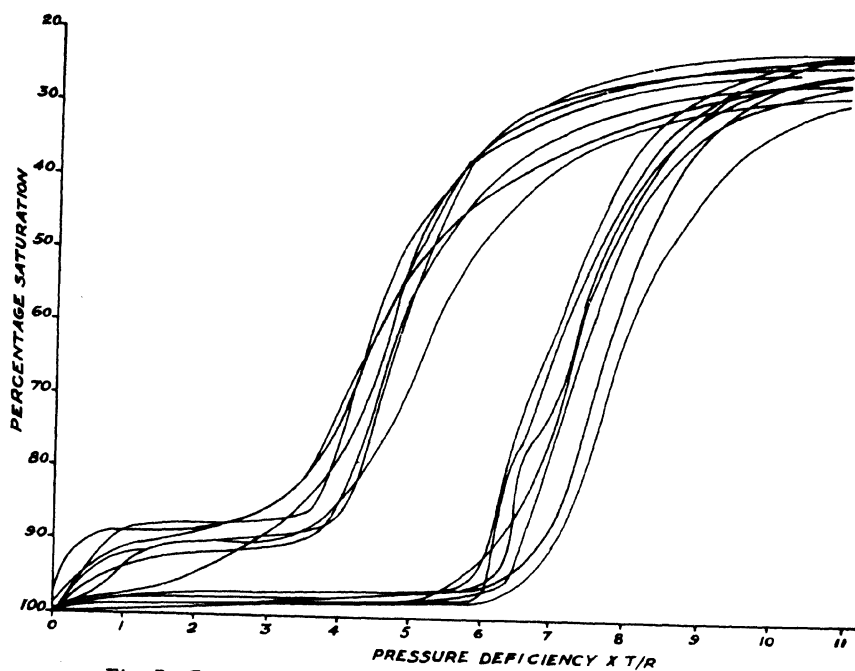



Fig. 7. Pressure Deficiency-Percentage Saturation Curves of Graded Silt Samples

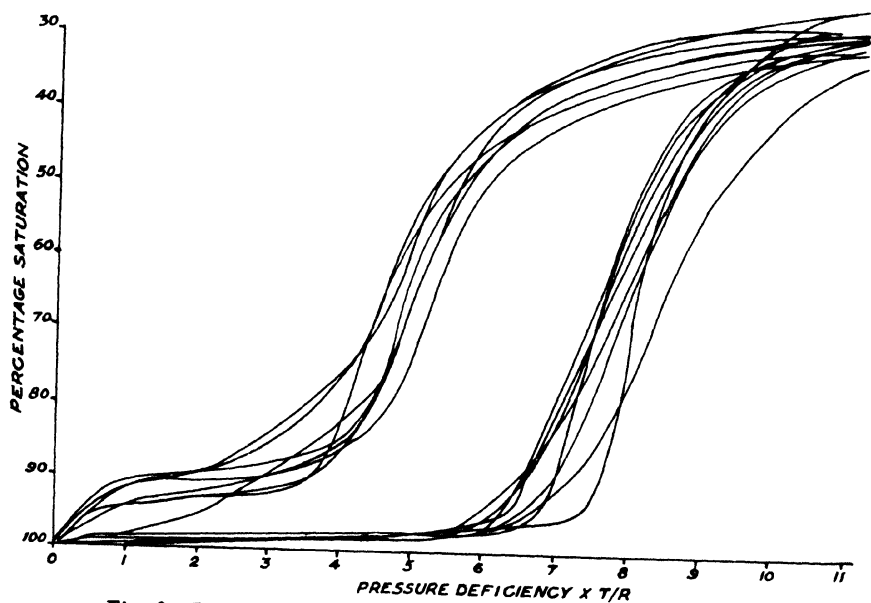



Fig. 8. Pressure Deficiency-Percentage Saturation Curves of Natural Silt Samples

tained for a number of graded silts (Figure 7) and also for a number of natural silts (Figure 8). In the latter case r was taken as mean radius as calculated from their size distribution curves. In Table 6 are given the pressure deficiency values for the three stages of moisture as interpolated from the pressure-saturation curves.

The agreement between the different values in both cases is as good as could be expected. The introduction of "mean diameter"

TABLE 6. Pressure deficiency values for the three stages of moisture in graded and natural silts.

No.	Mean diameter (mm)	Capillary stage	Funicular stage	Pendular stage
		Graded silts		
1	.44	4.2	6.4	11.8
2	.40	4.1	6.5	12.2
3	.39	4.4	6.4	12.0
4	.35	3.9	6.5	11.4
5	.32	4.1	6.5	11.4
6	.28	3.8	6.2	10.4
7	.27	4.1	6.2	12.1
8	.24	4.1	6.2	11.5
9	.23	4.2	6.4	11.2
10	.17	4.2	6.7	11.2
11	.13	4.2	6.5	11.4
		Natural silts		
13	.32	4.0	6.2	12.2
14	.23	4.0	6.9	12.5
15	.21	4.1	6.9	12.5
16	.15	4.1	6.8	11.2

has brought the conception of soil moisture in the "ideal soil" into line with natural soils, and thus has bridged the gap which long stood in the way of the practical application of results arrived at from theoretical considerations. The abnormally high theoretical values of capillary rise in soils based on the percentage of smallest particles, which could not be realized in practice and which ultimately led to the rejection of the capillary hypothesis, must be modified in the light of these experiments. The estimation of mean diameter in the case of soils should also assume greater importance. In fact, this hitherto unknown constant should be given prominence among single-value soil constants. It will not only impart a more precise meaning to the elusive factor known as soil texture, but afford a better insight into the exact relation between soil and moisture distribution.

It is clear from the foregoing that within the hysteresis loop the relation between the pressure deficiency and percentage saturation is unique for any given sand. Starting from saturation, on the application of gradually increasing pressure deficiency the mois-

ture percentages pass through a series of decreasing values which can be represented by a smooth curve and which can be reproduced and are characteristic for any particular sand under examination.

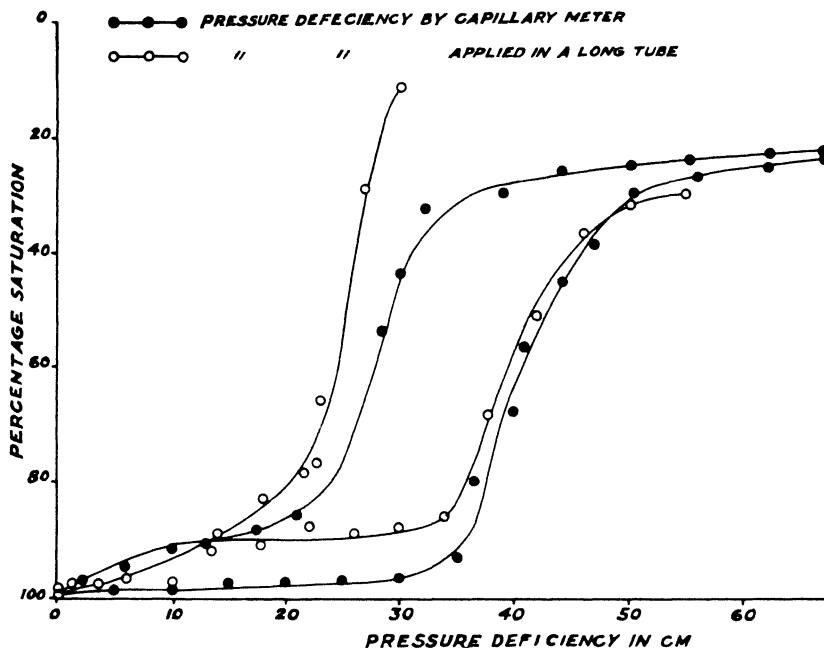



Fig. 9. Pressure Deficiency-Percentage Saturation Curves Determined by Capillarimeter and under free Drainage and Capillary Suction (Mean Diameter = 0.265mm)

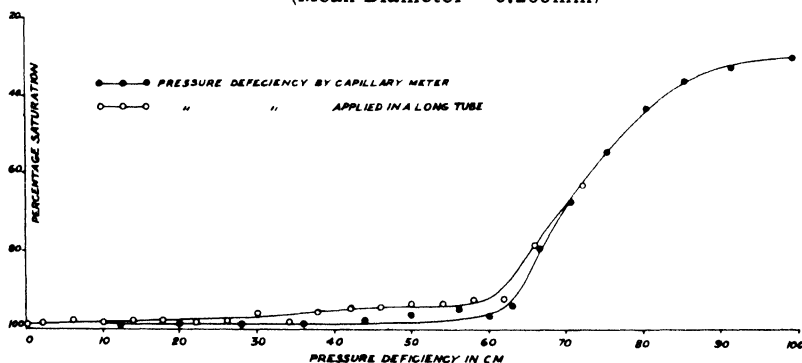



Fig. 10. Pressure Deficiency-Percentage Saturation Curves Determined by Capillarimeter and under free Drainage (Mean Diameter = 0.138mm)

Obviously, this relation expresses the moisture distribution in a vertical column under free drainage. In order to see if it is actually so, a number of glass tubes were packed with samples of sand and flooded with water. They were then allowed to drain away freely. Four-centimeter sections of the tubes were cut off and moisture content determined in each section. Typical curves of

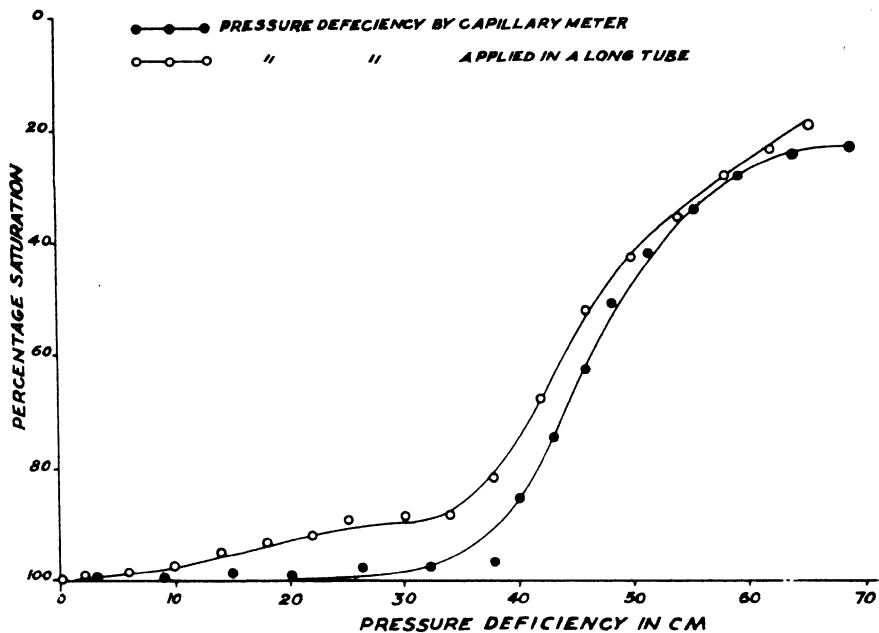



Fig. 11. Pressure Deficiency-Percentage Saturation Curves Determined by Capillarimeter and under free Drainage (Mean Diameter = 0.217mm)

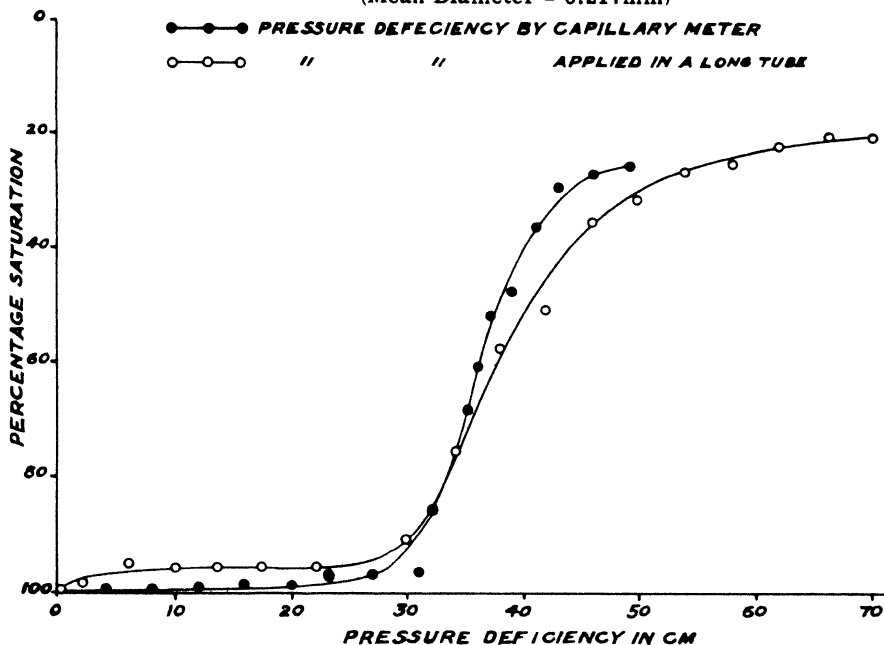



Fig. 12. Pressure Deficiency-Percentage Saturation Curves Determined by Capillarimeter and under free Drainage (Mean Diameter = 0.237mm)

this nature are shown in Figures 9-13, along with the values determined with the help of the capillarimeter. The agreement is remarkably close considering the nature of the substances.

The experiment was repeated with a number of sands; in every case the results of moisture distribution obtained under free drainage were almost identical with those obtained with the capillarimeter. This simple instrument can, therefore, serve a very useful purpose in predicting the moisture distribution in a sand column. A moment's reflection will show that just as the falling moisture curve represents the conditions under drainage, the rising curve of the hysteresis loop should indicate the moisture distribution under capillary rise. For an experimental verification of this

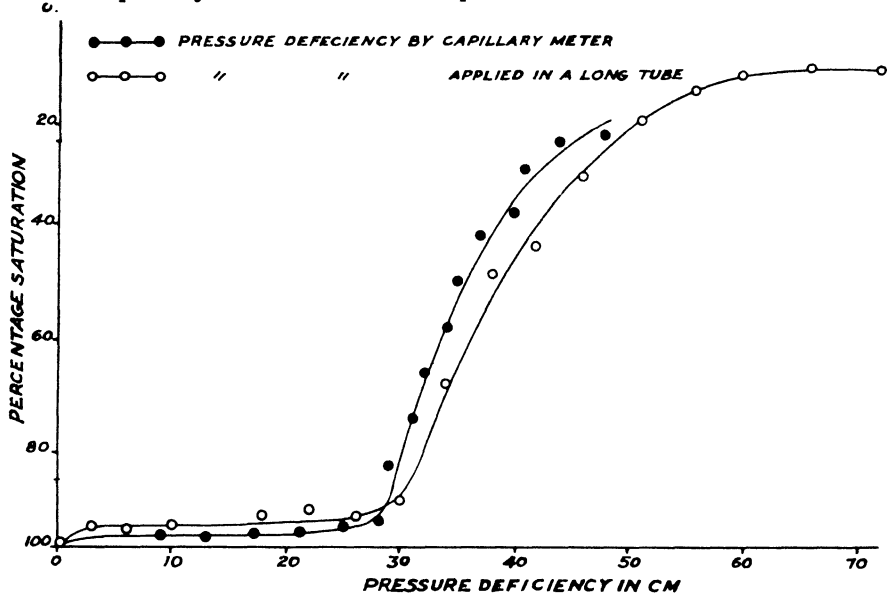



Fig. 13. Pressure Deficiency-Percentage Saturation Curves Determined by Capillarimeter and under free Drainage (Mean Diameter = 0.33mm)

supposition, a sand column contained in a glass tube was held vertically in a shallow basin of water. After 15 days, when the rise in the liquid column has stopped, the tube was cut into two-centimeter sections and the moisture content determined. The moisture distribution expressed in terms of percentage saturation plotted against pressure deficiency (capillary height) is shown in Figure 9. along with the rising curve for the same sand determined by the capillarimeter. The agreement between the two sets of values is as good as could be expected, leaving no doubt that the capillarimeter can be used for predicting the behavior of a silt both under free drainage and under capillary rise. The practical importance of this simple apparatus, therefore, needs recognition.

The application of the concept of mean diameter in the case of soils is not so simple as it might appear at the first sight. The

absence of aggregates or compound particles in sands and silts introduces no complication, and a sample examined in the laboratory may safely be relied upon to give the same results as the material *in situ*. The difficulty in the case of soils is twofold: the state of aggregation of the soil *in situ* may be quite different from that of the powdered and sifted soil sample examined in the laboratory. Besides, the laboratory sample, when brought into contact with water, will have a tendency to disperse and give out fine particles which may get into the interstices and thus reduce the pore size. Such a tendency may be quite absent in soil *in situ*.

The mean diameter of the soil itself can be considered from two angles. If the "ultimate mechanical analysis" is taken as the basis of calculations, the mean diameter would be different from that obtained when the results are computed from the "aggregate mechanical analysis" without dispersing the soil. This aspect of the question has been discussed in Part II. In fact, the state of aggregation has been defined therein, as the ratio between the two diameters, with and without dispersion. This being so, it becomes problemetical which of the two would be operative in influencing the maximum capillary pull given in Table 1C, it is evident that the maximum capillary force actually determined lies somewhere between the calculated values for mean diameters at maximum dispersion and without dispersion.

The fundamental relationship between pressure deficiency and percentage saturation of capillary pores can be established with liquids other than water, and the values of maximum capillary force conforming to mean diameters have already been shown to agree with those calculated from size distribution curves (Tables 4 and 5). It remains to be seen if the complete moisture distribution curve conforms to the pattern demanded by theory. To establish the fundamental relationship between pressure deficiency and percentage saturation of capillary spaces with liquids other than water, experiments were first made on a sample of sand having a mean diameter equal to 0.4 mm in the usual way. The results are plotted in Figure 14. The total pore space was taken as 31%. It will be seen that the curves obtained in the case of water, alcohol, aniline, benzene, as well as an alcohol-water mixture, are more or less superimposed, and the three critical values with their sudden changes of moisture distribution as well as the hysteresis effect are similar in every case. With kerosine, however, the curve is somewhat different, although it resembles the other curves in showing the break point at about the same critical value. But the subsequent loss of liquid is by no means so sudden and the movement of liquid continues with increase in pressure deficiency as far as 30 T/r. This may have something to do with the differences in the wetting powers of the various liquids. Experiments were next made with a black cotton soil (P.C.13) containing 52% clay. The results are plotted in Figure 15.

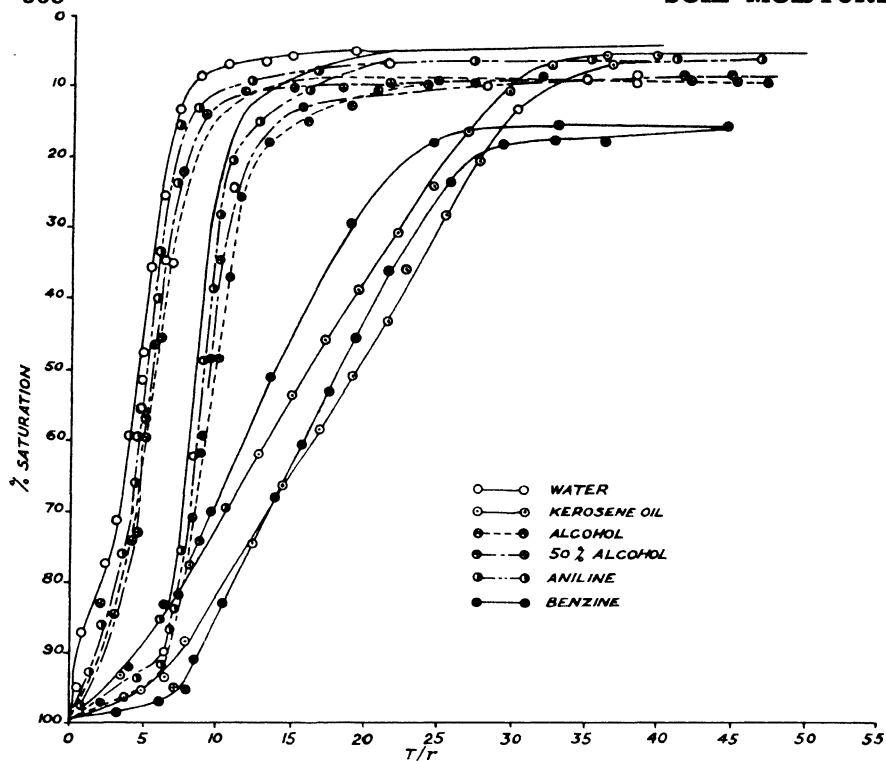



Fig. 14. Pressure Deficiency-Percentage Saturation Curves Determined by using Different Liquids (Mean Diameter = 0.40mm)

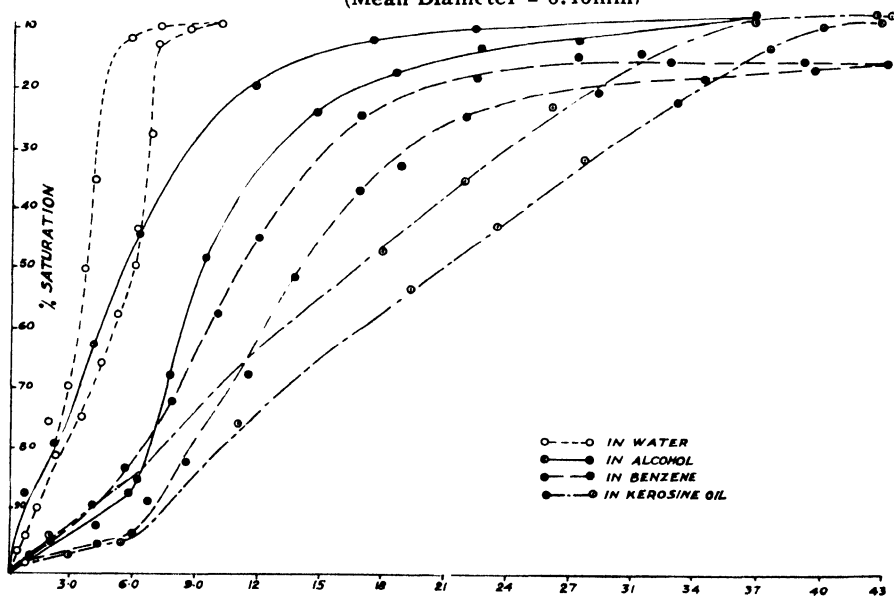



Fig. 15. Pressure Deficiency-Percentage Saturation Curves of P.C. 13 Soil Using Different Liquids

In the case of water the soil particles yield some liquid at every increase of pressure deficiency, and a considerable amount of liquid is squeezed out long before the first critical value of pressure deficiency is reached. This phenomenon very likely is due to the existence of compound particles in soils. In sands every particle is a rigid unit and water can exist only in the interstices. In the case of soils the compound particles form larger interstices; the moisture is held not only in those, but in the finer ones, between the primary units of which the aggregates are formed. The larger interstices, while emptying, draw water from the smaller capillaries of the compound particles, resulting in the squeezing out of larger amounts of water than would be the case with rigid particles of sand. At the first critical pressure deficiency, however, the curve shows a well defined point of inflection, as demanded by

TABLE 7. Heat of wetting of soil P.C. 13 with different liquids.

Liquid	Heat of wetting (calories)
Water	10.9
Alcohol	10.0
Benzene	6.14
Kerosine	3.14

theory. The curves obtained in the case of alcohol, benzene and kerosine show increasing deviations from the theoretical curve in the sense that the movement of the liquid continues much further than the critical pressure deficiency (12.1 T/r). although the first break in the case of all liquids is noticed at about the same point. That is why this value conforms to the mean diameter in every case.

It appears that beyond this break point the curves show greater and greater deviations from one another as well as from the ideal curve; the emptying of capillaries progresses differently in different liquids, the movement of liquid continuing in all cases other than water, even beyond the critical value of pressure deficiency (12.1 T/r) at which the liquid movement should have practically stopped. It is worth noting that while in the case of sand particles, only kerosine showed this anomalous behavior, benzene and alcohol exhibit it in soils. The capillary spaces concerned in a soil are naturally much finer than in sand and therefore the movement of these liquids is more restricted in soils than in sand. It is significant that the values for heat of wetting of this soil in the various liquids (Table 7) follow the same order as the deviation of their pressure deficiency curves from water.

The complete theoretical explanation of this deviation, however, is not forthcoming and is probably related to the contact angle or wetting power of the various liquids. It is significant in this connection that the pressure deficiency saturation curve with water assumes the appearance of the one given with partially wetting liquids when sand is coated with wax. This is shown in Figure 16, for a sand for which the normal curve with untreated sand is also shown.

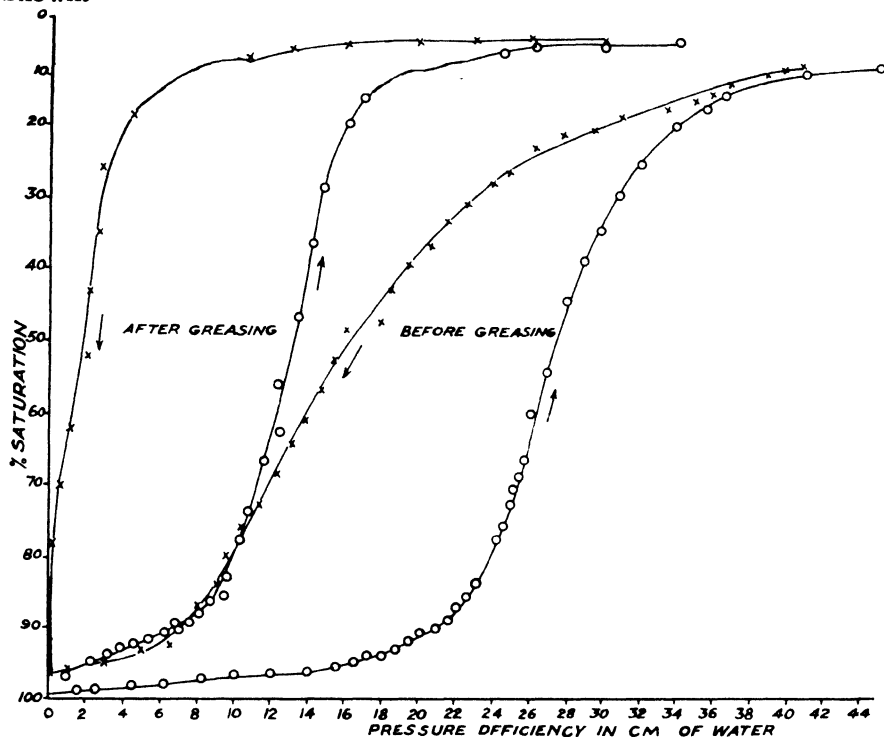



Fig. 16. Pressure Deficiency-Percentage Saturation Curves of a Sample of Sand (Mean Diameter = 0.46mm)

It has been shown in the foregoing that the relation $h = 1/D$ affords a very simple method of determining the mean diameter of sands and silts as well as soils by measuring the maximum pressure deficiency required to break the capillary column held by the particles. This is described by Haines as the "entry value". *i.e.*, the pressure deficiency at which the air enters the capillary pores. It is obvious, however, that any of the three critical values for pressure deficiency corresponding to the capillary, funicular, and pendular stages could be used for finding the mean diameter by interpolation from the pressure deficiency - percentage saturation curve. In Table 8 are given values for mean diameter determined from the three critical values of pressure deficiency, namely 4.1, 6.9 and 12.9 (T/r). by interpolation and calculated from mechanical analyses. The agreement between the different values is extremely good considering the nature of experimental material.

From the unique relationship between the diameter of particles (or the diameter of pores) and the critical points on the pressure

TABLE 8. Mean diameter of graded and natural sands interpolated from pressure deficiency curves and determined from size distribution curves.

No.	Mean Diameter Mechanical analysis	Capillary stage (cm H_2O)	Calculated Diameter (mm)	Funicular stage (cm H_2O)	Calculated Diameter (mm)	Pendular stage (cm H_2O)	Calculated Diameter (mm)
1	.44	12.4	.50	22.0	.47	40.0	.48
2	.40	13.5	.458	24.0	.434	46.0	.42
3	.39	14.8	.42	24.0	.434	47.0	.41
4	.35	16.0	.387	28.8	.36	50.0	.39
5	.32	17.2	.36	30.0	.34	54.4	.36
6	.27	21.5	.29	35.0	.30	65.0	.30
7	.28	22.5	.28	34.8	.30	67.0	.28
8	.24	26.0	.238	40.0	.26	72.0	.26
9	.23	29.0	.214	47.0	.22	79.2	.24
10	.17	36.5	.17	63.0	.16	99.3	.19
11	.13	51.0	.12	86.0	.12	128.0	.15
			Natural sands				
12	.32	15.0	.40	28.0	.36	55.0	.34
13	.23	24.5	.25	47.0	.22	77.0	.26
14	.21	30.0	.206	52.0	.20	84.0	.22
15	.15	39.0	.158	68.0	.15	110.0	.17

TABLE 9. Mechanical analysis of a natural sand determined by the siltometer

Diameter (mm)	Summation % interpolated from summation curve	Distribution (%)	Corresponding mean diameter (mm)	Pressure in terms of cms water at start of emptying	Pressure deficiency after emptying (cm Hg)
.06	0.0	5.0	.08	125.0	200.0
.10	5.0	5.0	.12	83.0	132.8
.14	10.0	26.0	.16	62.5	100.0
.18	36.0	26.0	.20	50.0	80.0
.22	62.0	19.2	.24	42.0	67.0
.26	81.2	10.8	.28	36.0	57.6
.30	92.0	4.8	.32	31.0	49.6
.34	96.8	1.1	.36	28.0	45.0
.38	97.9	0.9	.40	25.0	40.0
.42	98.8	0.2	.44	23.0	36.8
.46	99.0	0.4	.48	21.0	33.6
.50	99.4	0.4	.52	19.0	30.4
.54	99.8	0.2	.56	18.0	29.0
.58	100.0				

deficiency - percentage saturation curve for a silt, it should be possible to calculate this relation theoretically from the size distribution of particles in a given silt. The following example will

make this point clear. A natural silt had the following mechanical analysis as determined by the siltometer (Table 9).

The values of summation percentages were read out from the summation curve at regular intervals of diameter. The distribution percentages of various sizes were obtained by difference by assuming particles of a fraction to correspond to a size which is the mean of the values considered to be the upper and lower limits for that fraction. For example, if the summation percentage of 0.14 mm is 10% and that for 0.18 mm is 36%, the distribution percentage of 0.16 mm is taken as 23%, and so on.

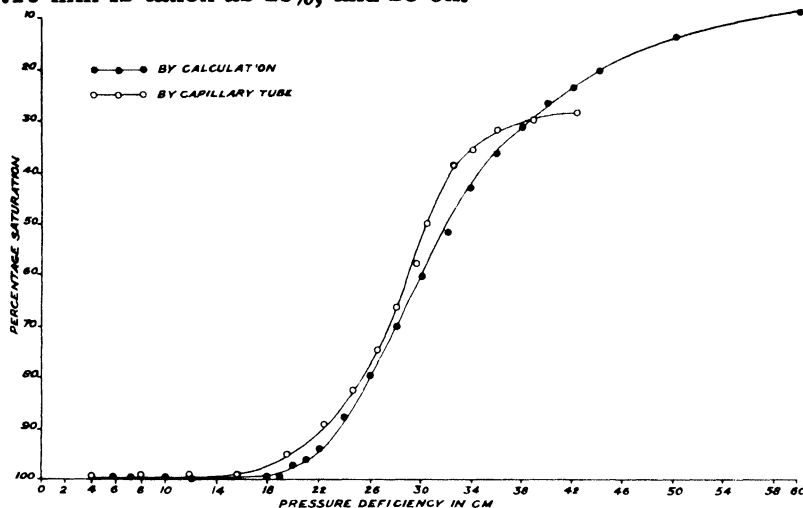



Fig. 17. Pressure Deficiency-Percentage Saturation Curves of a Sample of Sand Calculated from its Mechanical Analysis and Determined by the Capillarimeter (Mean Diameter = 0.40mm)

Now on reference to pressure deficiency - percentage saturation curves (Figures 7 and 8) it will be seen that emptying of the capillaries in almost all cases, irrespective of particle size, starts at 6.5 T/r and is completed at 10.5 T/r. Substituting the value of T and r it is possible to calculate the values of these two critical pressure deficiencies in term of centimeters of water for each particle size. These values are also included in Table 9, against each mean size.

It will be seen that up to 18 cm pressure deficiency no water is given out at all, and percentage saturation remains 100. Between 18 and 29 cm percentage saturation falls by 0.2% only, on account of the particles of 0.56 mm diameter. But when pressure deficiency has reached a value of 19 cm of water, particles averaging 0.52 mm would also begin to lose water, and percentage saturation on account of these particles would fall further by 0.4% between 19 and 30.4 cm pressure deficiency, and so on. In this way pressure deficiency - percentage saturation curves can be drawn from the results of mechanical analysis. These results are given in Table 9 and plotted in Figure 17, along with the curve determined experi-

mentally for the same sample. The agreement between the two curves is remarkably close, emphasizing once more the correctness of the capillary conception of soil moisture.

A word about an apparent anomaly in the two curves below 30% saturation. The theoretical curve extends beyond the point, whereas the experimental curve has stopped on account of the break in the continuity of the moisture film. It must be understood that there is no theoretical limitation to the application of pressure deficiency beyond the 30% saturation point. The calculated curve, therefore, represents the true state of affairs if the pressure deficiency could be applied by a more refined technique than is possible with the method. The theoretical supposition of complete evacution, though not realized practically, is essentially sound, and the complete agreement in the two curves up to the limiting point indicates that larger capillaries in contact with those of smaller diameter are as a matter of fact undergoing complete evacuation, until the moisture has receded to the smallest capillaries and the film continuity is broken. At this point the experimental curve ends abruptly, though the theoretical values can be calculated beyond, up to complete dryness. The asymptotic nature of the theoretical curve not only indicates a very high value of pressure deficiency of this magnitude, but brings out the wedge-shaped nature of the capillary cells resulting in extremely small radii in the final stages of evacuation.

CHAPTER IV

HYGROSCOPIC MOISTURE

Moisture absorbed in the vapor phase from a humid atmosphere by dry soil is called hygroscopic moisture. The amount of water thus absorbed obviously depends on the humidity of the atmosphere to which it is exposed: the higher the humidity, the greater the absorption. From an atmosphere at 100% saturation, the absorption of moisture is naturally maximum; this is known as the hygroscopic coefficient, a term introduced by Hilgard in 1859. It is defined as the percentage of moisture (on an oven-dry basis) that a soil holds when in equilibrium with an atmosphere saturated with water vapor. It was much used in America at one time as a "single-value" soil constant, although considerable trouble is involved in its accurate determination. The difficulty of maintaining a saturated atmosphere was soon realized and several workers on the continent, notably Rodwald and Mitscherlich, suggested the use of 10% sulphuric acid which gave a relative humidity of about 96% at ordinary room temperature. This determination is referred to as the "hygroscopicity" of a soil and must not be confused with the "hygroscopic coefficient". In the American method the principal difficulties center around (a) the obvious necessity of accurate temperature control; (b) the provision of a saturated atmosphere; and (c) the slow attainment of even an approximate equilibrium in a reasonable time at ordinary temperature. In spite of the experimental difficulties mentioned above, a considerable literature sprang up on the relation between the hygroscopic coefficient of soils and their field characteristics. It has been much used for comparing and contrasting soils. The reader is referred to the papers by Alway and his colleagues, Briggs and Shantz, for information on this phase of the subject.*

Earlier workers obtained conflicting evidence regarding the effect of temperature on the hygroscopic coefficient. For instance, Knop, Schloessing, Amon, and von Dobeneck found a lower value for the hygroscopic coefficient at higher temperatures. This result, controverted by Hilgard on the ground of incomplete saturation of the atmosphere within the absorption vessel, was subsequently obtained also by Patten and Gallaghar. Later Lipman, Sharp and

Complete list of references given by the author in Jour. Agric. Sci. Vol. 15:272 (1925).

Alway, and Klein and MacDole made experiments which indicated that the hygroscopic coefficient increases with temperature. The existence of diametrically opposite conclusions, both reasonably well supported by experimental evidence, led the author to the conclusion that some important factor must have been imperfectly recognized or left altogether out of account.

An elaborate set of measurements was conducted in a thermostat of diameter 3 feet and height 1.5 feet, provided with an efficient stirring arrangement and temperature control. There were four galvanized iron absorption chambers 6 x 10 x 6 inches high. They were arranged radially and symmetrically in the thermostate, and the bottoms were provided with legs and hooks to hold them in a position 4 inches above an open-strip metal framework, which ran across the thermostate 6 inches from the bottom. An easy and thorough circulation of water was thus secured. The chambers were immersed in water within 1/2 inch of their outer rim. Their entire interior, including the under surface of the lids, was lined with thick pads of water-saturated filter paper, so that when the lid was in position the inside surface was completely covered. Sufficient water was then added to cover the bottom of the lined vessel. The outside of each lid was lined with a thick layer of felt. Access to one chamber without disturbing the others was obtained by having the wood cover for the thermostat in four quadrant sections, fitting together to cover the whole bath. Thick pads of cotton wool were spread across the bath over the absorption chambers before the cover was put on.

The weighing bottles for holding the soil were 1 7/8 inches in diameter and 1 1/8 inches high. Five grams of soil spread at the bottom formed a layer 2 to 3 mm thick. These bottles had special lids, consisting of a flat circular glass plate with a ground-in groove to fit the rim of the bottle. The advantage of this kind of lid is that four to five of them can be held one above the other in the right order in one hand and rapidly placed on the bottles, while the lid of the absorption chambers is lifted. The various soils used were air-dried, passed through a 1-mm mesh sieve, and kept in well corked stock bottles. The air-dry moisture content was very accurately determined in every case by drying over concentrated sulphuric acid in a vacuum desiccator.

Five grams of each soil were taken for hygroscopic measurements; each absorption chamber contained four weighing bottles resting over pieces of cork. To minimize errors due to the condensation of water vapor on the inside of the weighing bottles and on the soil itself, the lids were not taken off until the bottles had been in the absorption chambers for 30 to 45 minutes. After the bottles had acquired the temperature of the bath, a section of the wood cover was removed, the corresponding absorption chamber partially uncovered, and the lids quickly taken off. Before the lids were replaced on the bottles, they were brought to a temperature

slightly higher than that of the thermostat, so that no condensation of vapors could take place on their inner surface, which was actually noticed to occur when this precaution was not taken. The possibility of dew formation on the inside walls of the weighing bottles when the latter are cooling to the room temperature cannot be denied, as a certain amount of difference of temperature between the walls of the bottles and the soil does occur. However, the soil being actually in contact with the walls, such a difference of temperature is likely to be small. Moisture deposition was not noticed except in one or two isolated cases where further absorption was stopped.

The first set of weighings was done after 24 hours' exposure, the second after 48 hours. Subsequent weighings were done on alternate days, *i.e.*, after an interval of 48 hours. The time required for the whole set of weighings and replacement was a little more than an hour, each group of bottles occupying about 15 minutes. After each weighing the bottles were gently shaken, and tapped, to mix the soil and expose fresh surfaces. When no appreciable gain of moisture could be noticed on subsequent weighings, the bottles were taken out and at room temperature, put in a desiccator, containing dilute sulphuric acid giving 50% humidity. The soils were allowed to lose moisture for two days, during which time the thermostate was adjusted to another temperature. The soils were then taken out of the desiccator, weighed, replaced in the absorption chambers, and allowed to take up moisture as before. The equilibrium condition was again followed by drying in the desiccator and re-absorption of moisture at another temperature. Four different temperatures were employed: 15.0, 20.2, 25.0 and 29.7°C, and in addition some of the soils were subjected to a temperature of 35.6°C. The following conclusions regarding the effect of temperature on the hygroscopic coefficient of soils were drawn:

(a) Hygroscopic coefficient decreases with rise of temperature. The effect however, is not regular or progressive:

(b) The rate of moisture absorption increases with rise of temperature. At ordinary room temperature (15°C), at which most of the earlier work on the hygroscopic coefficient was done, the rate of absorption is so slow that equilibrium is not attained even after 20 days (Fig. 18).

In view of the time taken to reach even an approximate final value, and the uncertainty of the final value itself, it would appear that even with the careful and laborious technique described above, no satisfactory determination of the hygroscopic coefficient can be made, and most of the discrepancies in the earlier results are due to faulty technique.

In presenting these conclusions, it is important to remember that the greatest care was taken to make the experimental methods and technique as accurate as possible. For routine determination of

the hygroscopic coefficient the method described would be far too elaborate, although it is possible that it might be used in certain special investigations. In view of this one is driven inevitably to the conclusion that the hygroscopic coefficient is not possible in any rigid or quantitative sense.

Quite apart from the purely experimental difficulty discussed above, the conception of the hygroscopic coefficient as a physical constant for each soil is open to serious criticism, because the value obtained would have no simple physical significance; it might,

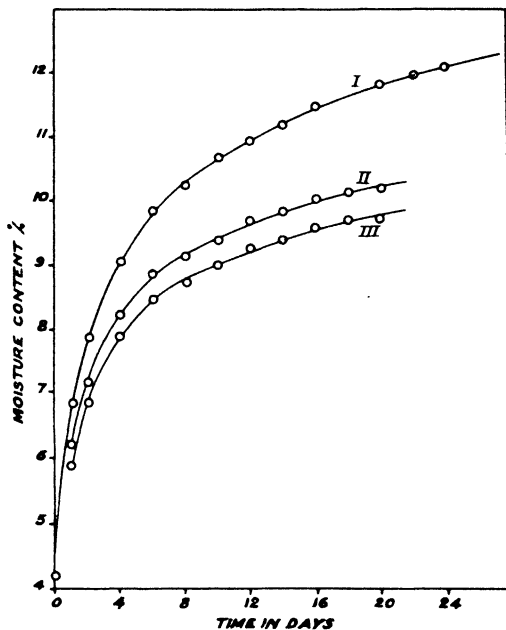



Fig. 18. Rate of Moisture Absorption from a Saturated Atmosphere

however, serve for empirical comparison of soils known to be of the same type.

The pore-space in soils is an assemblage of voids and irregular capillaries ranging from ultra-microscopic dimensions to the microscopic interstices between adjacent compound particles and the larger mineral fragments. The vapor pressure of soils at different moisture contents is controlled by the minute pores associated with the colloidal portion, and the larger voids have comparatively little influence. The study of the vapor pressure of moist soils is therefore of fundamental importance. The hygroscopic coefficient represents only one point on the vapor-pressure curve of the soil; moreover, this point is in the most uncertain region of the curve, for a very small change in the vapor pressure in this region will make a comparatively large difference in the equilibrium moisture content.

The vapor-pressure curve of a soil represents the percentage of

moisture when in equilibrium with atmospheres of different vapor pressures or relative humidities. Alternatively it indicates the vapor pressure that the soil will have with increasing moisture contents when confined in a closed space. The measurements are indirect and involve determination of the water content of soil samples in equilibrium with atmospheres of definite relative humidities, obtained by means of suitable sulphuric acid-water mixtures.

TABLE 10. Relation between normality, relative humidity, and density of sulphuric acid - water mixtures.

Serial No.	Normality	Relative Humidity (%)	Density 15°C/4°C
1	1.0	98.7	1.033
2	1.5	97.8	1.0505
3	2.0	96.8	1.0680
4	2.5	95.5	1.0835
5	3.0	94.2	1.0970
6	3.5	92.7	1.1120
7	4.0	90.9	1.1280
8	4.5	88.8	1.1440
9	5.0	86.7	1.1575
10	5.5	84.5	1.1705
11	6.0	82.2	1.1860
12	6.5	79.5	1.2010
13	7.0	76.4	1.2200
14	7.5	74.1	1.2320
15	8.0	71.3	1.2470
16	8.5	68.0	1.2660
17	9.0	64.8	1.2760
18	9.5	61.0	1.2920
19	10.0	57.4	1.3060
20	10.5	54.0	1.3200
21	11.0	50.7	1.3315
22	11.5	47.5	1.3460
23	12.0	44.3	1.3600
24	12.5	41.4	1.3740
25	13.0	38.4	1.3860
26	13.5	35.7	1.3980
27	14.0	33.0	1.4100
28	15.0	27.75	1.4370
29	16.0	22.70	1.4630
30	17.0	18.0	1.4920
31	18.0	13.7	1.5220
32	19.0	10.4	1.5470
33	20.0	7.6	1.5740
34	21.0	5.1	1.6000
35	22.0	3.4	1.6260
36	23.0	2.25	1.6540
37	24.1	1.55	1.6745
38	25.0	0.95	1.6970
39	26.0	0.55	1.7210
40	27.0	0.35	1.7440

To obtain mixtures of definite relative humidities it is only necessary to take the densities, and then compute the humidity from the relation between the two. In a chemical laboratory it is sometimes easier to determine normality instead of density: a single titration is all that is necessary. Density and relative humidity values at different normalities are given in Table 10. When plotted, these values give smooth curves from which intermediate values can be interpolated.

Three types of apparatus have been employed by the author and his co-workers for measuring the vapor pressure of soils (in terms

of relative humidity) at different moisture contents, or *vice versa*. These may be described as the air stream, the stirred chamber, and the vacuum desiccator methods. The measurements are indirect in all cases, and involve determination of the water content of soil samples in equilibrium with atmospheres of definite relative humidities, obtained by means of suitable sulphuric acid-water

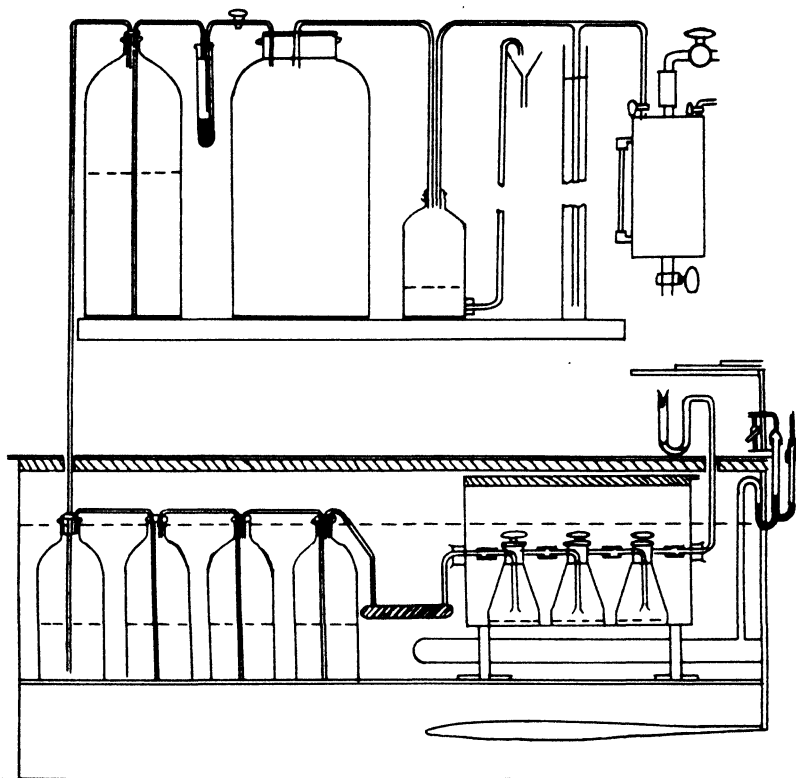



Fig. 19. Diagram of one Unit of Air-Stream Apparatus

mixtures. The actual values of these relative humidities are calculated by means of the data given in Table 10.

Air Stream Method

The air stream method is a development of that used by Wilson, with the addition of accurate temperature control. Steady streams of air are brought to the desired temperature and humidity, by passing them through a series of bottles containing sulphuric acid-water mixtures, and then over the soil samples in a special form of weighing flask. The apparatus consists of a number of units, one of which is represented diagrammatically in Figure 19, which shows the relative sizes of the various parts. A circular zinc bath, about 100 cm diameter and 45 cm deep is fitted with an efficient stirrer and a large toluene thermoregulator. The bath contains a

platform - built up of narrow vertical zinc strips to permit easy circulation of the water - supporting four inner water-tight chambers and the acid bottles. Each chamber contains six weighing flasks in two rows of three, and is covered with a zinc lid, heavily coated inside with felt. The entire bath is covered by wood lids heavily lagged on the lower sides. Within the bath there are arranged in a systematic manner eight separate units, each of four acid bottles and three soil weighing flasks. To avoid any risk of a spray being carried over from the acid, the air is passed through a glass tube packed with glass wool before entering the weighing bottles.

From the last weighing bottle the air escapes through a U-tube containing the same acid, to prevent back-diffusion. The weighing flasks have ground-in glass stoppers such that a fractional turn will completely seal the flask, while in the open position the air is led down toward the base of the flask, which is quite flat so that the samples can be spread out in thin layers. The walls of the flask are made vertical near the base to secure efficient circulation of air over the whole surface of the soil. The specific gravities of the acids show no significant change in concentration during the course of the experiment. Great care is necessary to secure accurate weighings of the flasks, especially when there is any large temperature difference between the bath and the balance case. The flasks are allowed to stand near the balance case for about half an hour before being weighed and a similar flask should be used as counterpoise. The air streams are obtained from a small pressure pump, provided with a reservoir and safety valve to keep the pressure constant.

From a large bottle eight separate tubes are led away through the eight series of acids. The difference in density of the various acids introduces different pressure heads, which are compensated by the introduction of an adjustable column of mercury. In this way the taps are needed only for the finer adjustments of the air streams and an equal distribution of air between the several series is obtained.

Weighings are made either daily or on alternate days and the equilibrium point taken as that at which the weights show a change of less than 1 mg (on a 5- or 10-gram sample) in two days.

Stirred Chamber

A 15-liter bottle containing 4 liters of sulphuric acid is fitted with a mercury seal so that both the atmosphere and the acid could be stirred continuously. Several weighing bottles containing soil samples are suspended simultaneously in the bottle. This apparatus is more convenient for determining the loss of water over concentrated sulphuric acid and can therefore be used for obtaining the initial water contents of the air-dry soils used in the air stream apparatus.

Vacuum Desiccators

Desiccators capable of holding vacuum for several days are used for the purpose. No temperature control is necessary, as the relative humidity of the soil and the acid is very little changed by the usual variations in temperature. Each desiccator should be capable of holding several squat weighing bottles with ground-in lids. Large quantities of the acid mixtures are made up and the acid in the desiccators renewed frequently. Before weighing, the air is let in through a small tube containing soda lime and cotton wool, preliminary experiments having shown that it is unnecessary to allow the air to enter through acid of the same humidity. Weighings are made on alternate days, and should show constant weights after the second weighing.

One of the principal difficulties in work of this type is the uncertainty attached to the term "dry soil". For ordinary moisture determinations, where the soil has initially a considerable percentage of water, drying in a steam oven is sufficient, since duplicates usually agree to within 0.1 to 0.2%. For experiments requiring a higher degree of accuracy it is better to define "dry" soil as that which shows no change in weight after exposure for two days over concentrated sulphuric acid in either the stirred chamber or the vacuum desiccator.

TABLE 11. Water content of an air-dry soil as determined by several methods.

(a) Air stream	(b) Stirred chamber	(c) Vacuum desiccator	Steam Oven
25°C	25°C	16°C	98°C
2.65	2.69	2.64	2.62
2.69	2.67	2.63	2.65
2.69	2.67	2.62	2.62
2.65	2.70	2.64	2.62

The experiments in general follow one of two courses, which may be referred to as "consecutive" determinations and "direct" determinations, respectively. In the former the same sample of soil is placed in turn over a number of acids of different relative humidities; in the latter a separate sample of air-dry soil is placed over each strength of acid. The water content of the soils in these direct determinations is obtained by exposing over concentrated sulphuric acid in the manner already described samples taken at the same time from the stock bottle, and computing the water contents at equilibrium by difference. The sampling error thus introduced is found to be small, as may be seen from Table 11, in which several methods of drying are compared.

In Figure 20 are plotted vapor pressure-water content curves of five soils to illustrate that they are all of the same type and show a pronounced inflection. The curves are flat for both very high and very low humidities, and thus show the difficulties involved in defining either the "dry" state or the "hygroscopic coefficient". As

the results given by the two methods agree very closely, either method can be reliably employed. Of the two, the desiccator method requires less attention and allows a greater number of determinations to be conducted simultaneously. The major portion of the work described in this volume is based on determinations carried out in vacuum desiccators.

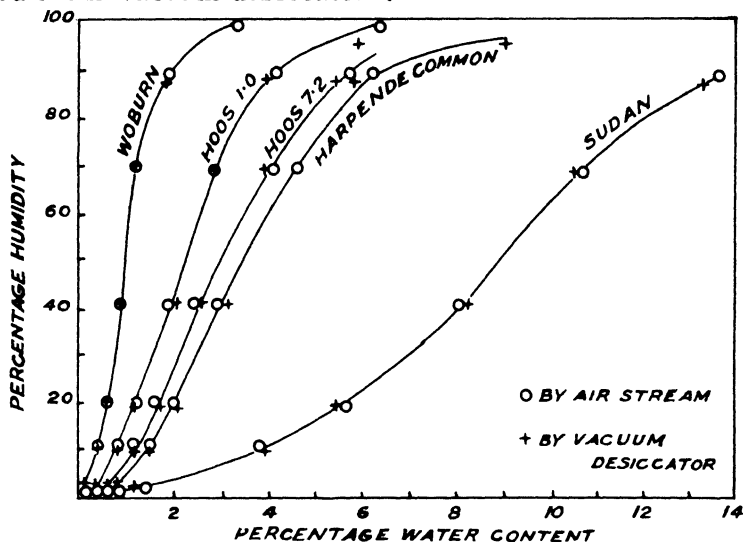



Fig. 20. Vapor Pressure Curves of Typical Soils

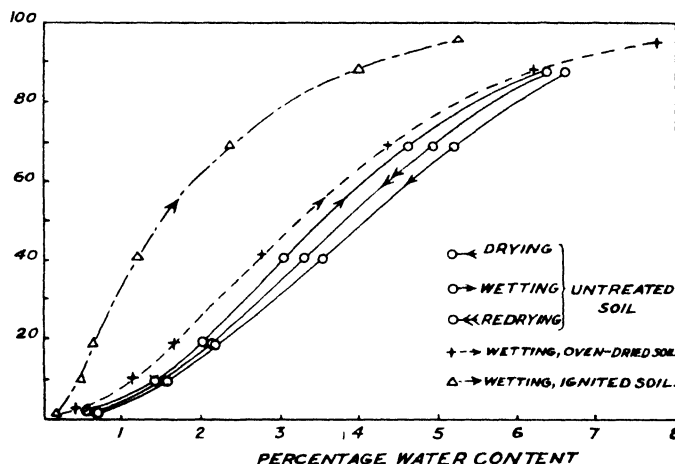



Fig. 21. Vapor Pressure Curves of Untreated, Oven-dried, and Ignited Soils

It is well known that materials with a capillary or colloidal structure exhibit hysteresis in their water relationships and that at equilibrium a material that has dried down to that state will contain more water than one that has reached it by absorbing water. Considerably lower water contents are shown by a sample of the same soil which has been dried previously over concentrated

sulphuric acid. In Figure 21 are plotted the results of a complete series of operations on a single sample of soil. From the air-dry state it was placed in a more humid atmosphere and then in turn through a series of dryings, wettings and redryings.

The most important conclusion that emerges from this study and which must be borne in mind is that the water contents for a given humidity are always higher when that humidity is reached by drying than when it is reached by wetting. From hundreds of vapor-pressure curves of all types of soils and other materials of diverse character, but possessing in common a capillary structure, the

TABLE 12. Water contents and relative humidities at different temperatures (direct determinations by air stream method.

Relative Humidity			Water content								
			A (Woburn)			B (Hoos 1.0)			F (Sudan)		
20°	30°	40°	20°	30°	40°	20°	30°	40°	20°	30°	40°
89.5	89.8	90.1	2.06	2.06	2.06	4.25	4.28	4.36	14.07	14.07	13.98
68.6	69.4	70.2	1.41	1.44	1.41	3.03	3.04	3.3	10.74	10.69	10.66
39.7	40.9	42.0	1.03	1.03	1.02	1.97	1.97	1.95	8.07	8.04	8.01
19.1	20.3	21.4	0.78	0.73	0.70	1.44	1.32	1.30	5.64	5.55	5.50
10.0	10.8	11.6	-	-	-	1.09	0.97	0.93	4.06	3.95	3.91
1.7	1.9	2.2	0.34	0.30	0.27	0.50	0.46	0.43	1.56	1.48	1.44

TABLE 13. Ratio of relative vapor pressure at 30° or 40° to that at 20° for constant water contents.

Humidity at 20° (%)	% humidity at 30° / % humidity at 20°			% humidity at 40° / % humidity at 20°		
	Soil A	Soil B	Soil F	Soil A	Soil B	Soil F
89.5	1.00	1.00	1.00	1.00	1.00	1.01
68.6	1.00	1.01	1.02	1.03	1.03	1.04
39.7	1.03	1.04	1.05	1.07	1.07	1.08
19.1	1.23	1.25	1.11	1.36	1.34	1.17
10.0	--	1.39	1.13	--	1.56	1.24
1.7	1.8	1.5	1.3	2.4	1.8	1.5

author has come to the conclusion that there is no exception to this rule. That this hysteresis effect is fundamental has been proved beyond doubt by the results of experiments that will be described later.

Vapor Pressure of Soils at Different Temperatures

Samples of three air-dried soils were brought to equilibrium with atmospheres of various humidities in the air stream apparatus at 20°C. The weighing flasks were then replaced with the stoppers closed, and the temperature of the bath slowly raised. After a sufficient interval for accurate adjustment of the temperature to 30°C, the air streams were passed again for several days. When equilibrium had been attained the experiment was repeated at 40°C. Table 12 gives the water contents for three soils at six humidities at 20, 30 and 40°C, together with the relative humidities of the atmospheres.

In order to facilitate comparison of the vapor pressure at different temperatures, the vapor pressures at 30 and 40°C were evalu-

ated by graphical interpolation of the data contained in Table 12 for the particular water contents recorded at 20°C. Table 13 contains the ratios of the vapor pressures at each of the temperatures 30° and 40° to those at 20° for soils of constant water content.

Table 13 brings out the interesting feature that in atmospheres of high humidity, the relative vapor pressure of soils is practically independent of the temperature, but that in atmospheres of low humidity it increases considerably with increasing temperature until, at the lowest humidity studied, the relative vapor pressure is almost doubled by a 20° rise. Shorter has subjected to a thermodynamic treatment some similar data obtained by Schloesing for

TABLE 14. Comparison of water contents for definite humidities at 96° C and 16° C (direct determinations in vacuum desiccators).

Humidity (%)	A (Woburn)		B (Hoos 1.0)		F (Sudan)	
	16°	96°	16°	96°	16°	96°
74	1.3	0.3	3.1	1.1	11.2	6.7
49	--	--	2.1	0.9	8.9	6.5
27	0.7	0.2	1.4	0.6	6.7	4.3
16	--	--	1.1	0.5	5.0	3.0
4	0.3	0.1	0.5	0.3	2.5	1.1

cotton and wool, and has been able to show that this increase of vapor pressure, or diminution of hygroscopic capacity with rise of temperature is a general property of hygroscopic substances, which absorb water with the evolution of heat.

A further illustration of this temperature effect was obtained in some approximate determinations at about 96°C. A vacuum desiccator, containing sulphuric acid of suitable strength and several soil samples, was placed in a large steam oven and the temperature slowly raised to the boiling point of water. After 24 hours the vacuum was released and the weighing bottles quickly removed, closed and weighed when cold. The errors in these determinations are considerable, but a comparison (Table 14) of the observed water contents with those obtained by interpolation to the same relative humidities from the data obtained at 16°C brings out the marked reduction in water absorption at higher temperature.

Effect of Initial Heating of the Soil on its Vapor Pressure Curves

Experiments on several soils showed that the water absorption values of oven-dried soils at all humidities were considerably less than those of soils dried over concentrated sulphuric acid at 25°C. This point may be illustrated by a comparison of the second and third columns in Table 15, or the corresponding wetting curves of the untreated and oven-dried soils in Figure 21.

This observation affords a further illustration of the permanent alteration resulting from heating soil. The loss of water from the air-dried soils happened to be the same in the steam oven as at

25°C over sulphuric acid, but the curves representing the subsequent absorption of water are appreciably different. Further, it will be observed that the curves are approximately parallel and are merely displaced. Figure 21 and Table 15 also include data for the same soil after ignition on a silica dish over a Bunsen burner. The ignited soil still shows considerable hygroscopicity, but the vapor pressure curve is of a different type, being concave over almost the whole range.

A more detailed study was made on samples of soil (E) which

TABLE 15. Water absorption by heated soils from moist atmospheres (consecutive determinations on soil E in vacuum desiccators).

Humidity (%)	25°	100°	109°	120°	130°	146°	170°	200°	Ignited
1.6	0.55	0.41	0.46	0.51	0.53	0.66	0.59	0.69	0.14
9.8	1.42	1.14	1.21	1.29	1.39	1.27	1.24	1.27	0.49
19.1	2.04	1.68	1.77	1.84	1.91	1.81	1.59	1.59	0.65
40.6	3.05	2.77	2.84	2.91	3.00	2.95	2.80	2.59	1.20
69.3	4.62	4.36	4.44	4.51	4.61	4.60	4.43	4.42	2.37
88.2	6.34	6.21	6.31	6.43	6.50	6.47	6.33	6.30	3.98
95.9	--	7.74	7.84	7.78	7.94	7.95	8.05	7.97	5.25
% loss on heating	3.87	3.87	4.02	4.19	4.37	4.81	5.03	5.47	8.11

were heated for 24 hours in a hot-air oven maintained at various temperatures up to 200°C. Table 15 also gives the percentage loss on heating the air-dried soil and the percentage absorption of water at various humidities in a consecutive series of determinations in vacuum desiccators. For comparison, Table 15 also includes similar figures for the same soil after drying at 25°C over concentrated sulphuric acid. In all cases the figures for the loss of absorption of water are expressed as percentages of the dried or heated material.

The results for the loss of weight on heating show a regular linear increase with increasing temperature (Figure 22). This relationship is strong circumstantial evidence that the main effect of heating (up to at least 200°C) in this instance is removal of strongly held water from hydrous substances and produces no great alteration of the fundamental structure of the soil. The loss of water is considerable. This soil had an initial moisture content of 3.87%, as determined by conventional drying at 100°C, and yet a further loss of 1.6% occurs on heating to 200°C. This result also emphasizes the need for a precise description of the standard adopted for the "dry" soil in any exact studies.

To obtain further information about the soils heated to 146°, 170°, and 200°C, they were subjected to a further series of consecutive dryings and rewettings with the results given in Figure 23. These heated soils also show considerable hysteresis. In addition it will be seen that whereas in the first wetting the three soils showed the

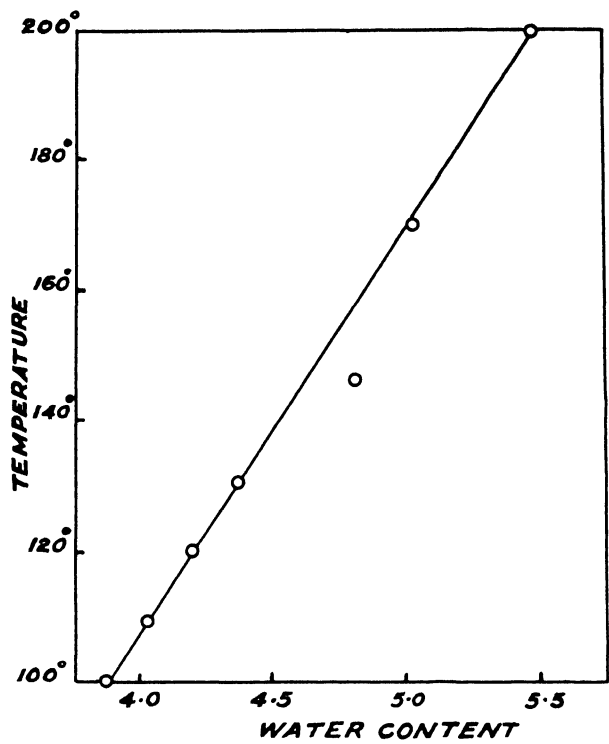



Fig. 22. Moisture Content of a Soil Determined by Heating to Different Temperatures

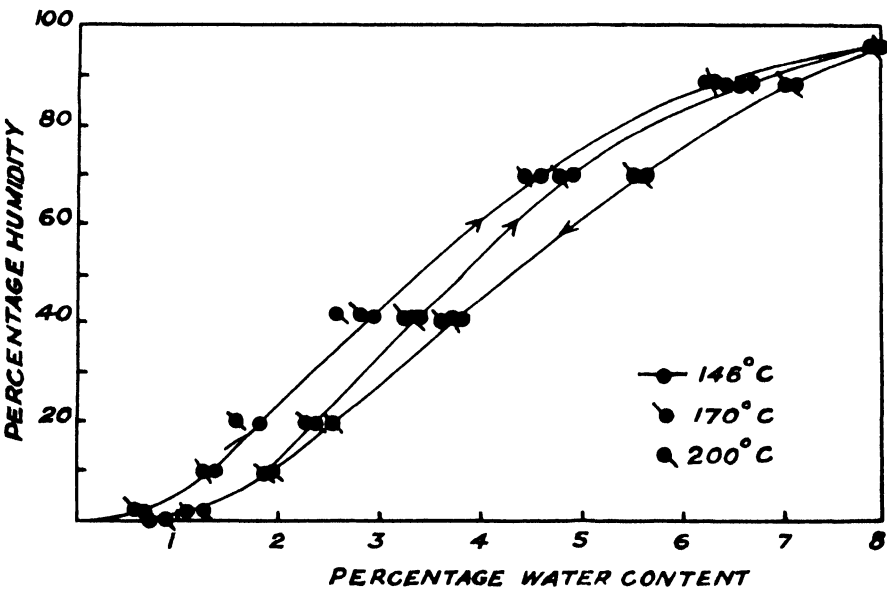



Fig. 23. Vapor Pressure Curves of a Soil Heated to Different Temperatures

slight systematic differences just discussed, the subsequent drying and rewetting gave substantially the same results for all three soils. Further, it is interesting to note that even after prolonged exposure over concentrated sulphuric acid the heated soils did not lose all the water they had taken up during the wetting process, but retained 0.70%, 0.71% and 0.86% for the soils heated to 146°, 170° and 200°, respectively.

The absorption of moisture at various humidities by a soil heated to still higher temperature is shown in Figure 24. A progressive decrease in hygroscopicity with increasing temperatures is apparent at all humidities.

The percentage of conventional clay (0.002 mm diameter) has an important bearing on the colloidal properties of soils, and the

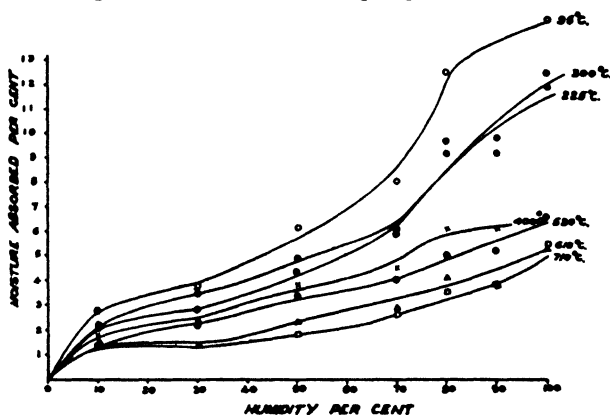



Fig. 24. Moisture Absorption at Different Humidities by Soil Heated to Various Temperatures

effect of heat on this factor is of interest. Clay was determined by shaking for 24 hours with sufficient NaOH to raise the pH value to 10.8. The results showed a progressive decrease in the clay content, which reached a minimum value at 400°C. It seems that the dehydration of clay at higher temperatures leads to a progressive fusion of clay particles, resulting in stable aggregates which cannot be disintegrated by ordinary methods of dispersion, and therefore cannot be distinguished from coarser fractions.

It is of interest to see whether decrease in clay content due to dehydration can be correlated with the decrease in hygroscopicity. The relation between clay and moisture absorption at various humidities is shown in Figure 25. Moisture absorption decreases with the decrease in the clay content, which diminishes as the temperature of ignition increases.

Vapor-pressure Relations of Soil and its Finer Fractions (Consecutive Determinations)

The finer fractions of the conventional mechanical analysis (clay, fine silt II, fine silt I, and silt) were separated by repeated sedi-

mentation in distilled water without previous acid treatment of the soil. Samples of each fraction and the original soils were exposed

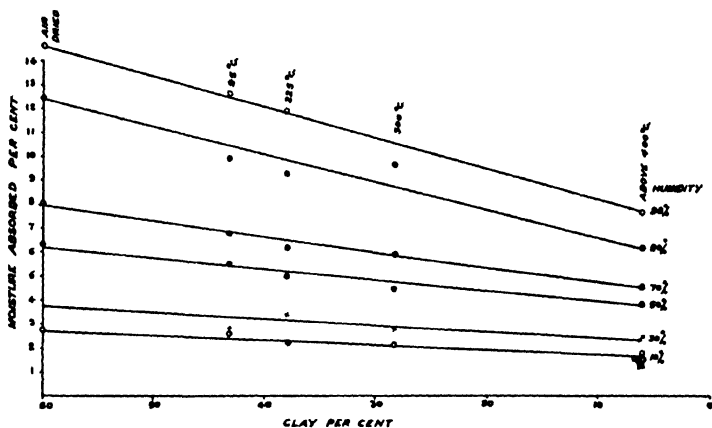



Fig. 25. Relation Between Clay and Hygroscopicity of Soil Heated to Various Temperatures

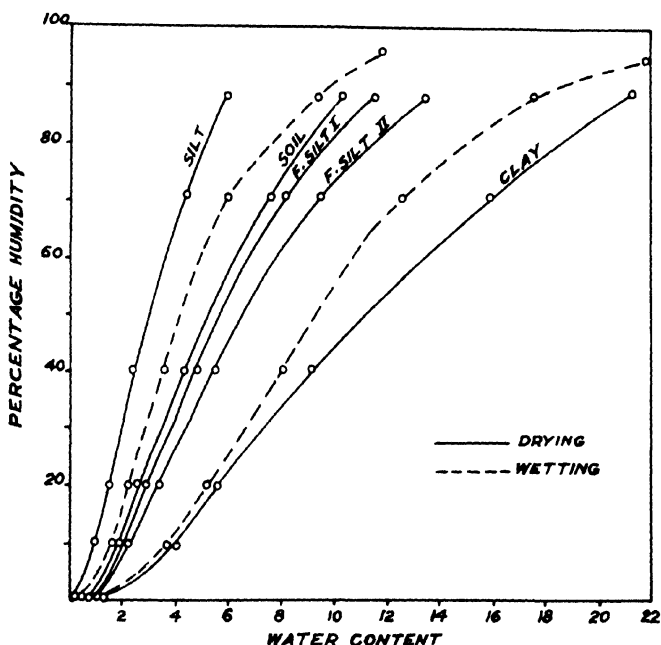



Fig. 26. Vapor Pressure Curves of a Soil and the Finer Fractions

in vacuum desiccators to an atmosphere of 88.2% humidity and then in turn to each of the lower humidities. The clay fraction and soil were then rewetted through the same series of humidities. Figure 26 shows that the soil fractions show substantially the same type of

curve as the soil, and the order of the curves is that to be expected from the mean diameters or specific surfaces of the samples. Whereas in many other physical properties the clay fraction differs sharply from coarse material, its vapor-pressure curve differs only slightly from the other soil fractions, although the absolute amounts of water taken up are of course much greater.

From an examination of the vapor-pressure curves of soils and fractions, it will be noted that the water content for any relative humidity increases with the amounts of clay. Several attempts have been made by soil workers in the past to correlate hygroscopic coefficient with the mechanical composition of soils. It was soon recognized, however, that these empirical formulas had only a limited applicability, and a rough correlation between mechanical composition and hygroscopicity was all that could be reasonably expected.

The difficulty in finding a more rigid relationship lay in the very nature of things. Methods of determining clay (which is considered to be mainly responsible for moisture absorption) as well as hygroscopic coefficient were extremely faulty. With the introduction of newer methods of mechanical analysis of soils, clay can be determined with great precision. Moreover, vapor-pressure curves gave a more comprehensive picture of the hygroscopicity of soils than had previously been possible. From the nature of these it will be clear that the "dry point", corresponding to zero humidity, is quite as indefinite as the equilibrium point with saturated atmosphere. By adopting 10% humidity equilibrium value as the "dry" basis, we can be sure of greater precision in the determination of this reference point.

On this basis, the vapor-pressure curve up to 70% humidity being a straight line passing through the origin, the determination of a single value will enable us to interpolate hygroscopicity at any other humidity between 10 and 70%. The hygroscopicity on the basis of 10 to 70% humidity shows an excellent correlation with clay content in different soils. Indeed it is possible to calculate the percentage of clay (0.001 mm diameter) in a given soil by determining its hygroscopicity between 10 and 70% humidity.

It was previously stated that moisture content corresponding to a given humidity is always higher when that humidity has been reached by drying than when it is reached by wetting. To work out the correlation between hygroscopicity and clay content, both the values were determined for 57 soils. The correlation coefficient when the equilibrium values were reached by drying was found to be 0.996, and when they were reached by wetting the correlation was 0.993. Both these values are highly significant. The following relations hold good between clay (0.001 mm) and hygroscopicity, (H):

<u>Drying</u>: Clay = 8.04 H + 1.02
<u>Wetting</u>: Clay = 8.41 H + 2.8

In Table 16 are given the calculated values of clay, that is, the mean of the drying and wetting hygroscopicity values.

The agreement between the calculated values and those found by direct determination with the pipette method is as good as could be

TABLE 16. The relation between hygroscopicity and clay content.

Soil	H (%)	Clay (0.001 mm) Calc. (%)	Clay (0.001 mm) Found (%)	Difference (%)
		Punjab Soils		
P.C. 4	0.79	8.4	10.5	+ 2.1
P.C. 5	0.56	6.5	9.6	+ 3.1
P.C. 7	1.92	17.9	17.5	- 0.4
P.C.16	0.52	6.1	5.4	- 0.7
P.C.34	0.68	7.4	8.1	+ 0.7
P.C.35	1.75	16.3	16.9	+ 0.6
P.C.36	0.74	8.0	9.0	+ 1.0
P.C.47	1.01	10.2	12.8	+ 2.6
P.C.48	1.10	10.9	15.7	+ 4.8
P.C.53	0.85	8.8	15.2	+ 6.4
P.C.54	0.15	3.1	2.6	- 0.5
		U.P. Soils		
P.C.17	1.00	10.1	8.9	- 1.2
P.C.24	0.83	8.7	5.5	- 3.2
P.C.57	0.60	6.8	1.9	- 4.9
P.C.58	2.12	19.3	11.7	- 7.6
P.C.59	0.81	8.6	7.8	- 0.8
P.C.60	1.24	12.2	4.8	- 7.4
		C.P. Soils		
P.C.13	6.32	53.9	56.5	+ 2.6
P.C.28	4.35	37.7	42.8	+ 5.1
P.C.29	6.34	54.0	61.1	+ 7.1
P.C.30	6.72	57.1	53.5	- 3.6
		Bombay Soils		
P.C. 2	6.04	51.6	56.1	+ 4.5
P.C. 3	6.69	56.7	61.2	+ 4.5
P.C.38	5.59	47.8	50.9	+ 3.1
P.C.39	1.30	12.5	7.2	- 5.3
P.C.40	1.26	12.3	11.6	- 0.7
P.C.41	6.39	54.4	51.6	- 2.8
P.C.42	7.01	59.5	54.4	- 5.1
P.C.46	6.58	56.0	55.9	- 0.1
		Bihar Soils		
P.C. 1	0.31	4.5	6.4	+ 1.9
P.C.43	1.90	17.5	16.2	- 1.3
P.C.44	0.37	5.0	5.4	+ 0.4
P.C.45	0.78	8.3	8.9	+ 0.5
P.C.52	0.82	8.6	10.5	+ 0.9
		Bengal Soils		
P.C. 6	1.79	16.6	25.2	+ 8.6
P.C.37	0.45	5.6	2.8	- 2.8
P.C.49	0.73	24.3	26.7	+ 2.4

TABLE 16 (Contd.)

		Madras Soils		
P.C. 8	2.59	23.2	22.5	- 0.7
P.C. 9	1.51	14.3	15.9	+ 1.6
P.C.10	3.79	33.0	32.2	- 0.8
P.C.11	3.26	28.6	29.3	+ 0.7
P.C.14	2.51	32.5	16.6	- 5.9
		Assam Soils		
P.C.12	0.60	6.8	8.8	+ 2.0
P.C.15	1.92	17.6	17.2	- 0.4
		Burma Soils		
P.C.18	1.35	13.2	15.1	+ 1.9
P.C.20	0.34	4.7	5.3	+ 0.6
P.C.21	1.33	12.8	9.7	- 3.1
P.C.22	1.02	10.3	11.9	+ 1.6
P.C.23	0.98	9.5	8.9	- 0.6
		Travancore Soils		
P.C.31	2.17	19.7	20.9	+ 1.2
P.C.32	6.81	57.7	56.3	- 1.4
		Mysore Soils		
P.C.26	3.11	27.4	22.4	- 5.0
P.C.27	6.35	54.1	52.6	- 1.5
		Sind Soils		
P.C.55	0.96	9.8	6.8	- 3.0
P.C.56	1.37	13.2	8.7	- 4.5
		N.W.F. Soils		
P.C.50	1.47	13.9	13.8	- 0.1
P.C.51	1.08	10.7	9.7	- 1.0

expected from a highly complex body like soil, when the errors involved in the measurements are considered. The few soils that show rather serious discrepancy are invariably abnormal types. Soil P.C. 6 is a highly acid soil, entirely barren; P.C. soils 53, 56, 57, 58 and 60 are highly alkaline barren soils containing free Na_2CO_3.

The correlation between clay and hygroscopicity, though excellent, is still no more than empirical. It is devoid even of practical utility for it is much easier to determine clay content than hygroscopicity at 10 to 70% humidity.

CHAPTER V

RELATION BETWEEN ULTRA-MECHANICAL ANALYSIS AND MOISTURE ABSORPTION AT VARIOUS HUMIDITIES

For a fuller comprehension of the data to be presented in this preceding chapter it would be well to summarize the basic relationship between the diameter of particles, the relative humidity of the water held in their interstices and its free energy. The latter is represented by the symbol pF, which is the logarithm of the height in centimeters to which water would rise in a capillary against the force of gravity by surface tension effect, or the negative pressure to which it must be subjected to draw out the water held in it. This is given in Table 17.

The extremely simple relationship between pF and particle diameter has already been elaborated. Since pF is numerically equal to pD, in the mechanical analysis of soils it is immaterial whether one plots the logarithms of particle diameters (pD) or the logarithm of the maximum height to which water can rise. The resulting summation curves will be identical.

It might be pointed out that values corresponding to particles of 10^{-7} cm diameter (pF7) are of theoretical interest only, as the diameter of the capillaries formed by the particles is smaller than that of water molecules, and the relative humidity also corresponds to a state of complete dryness. Moreover, conventional clay (particles of 0.001 mm diameter corresponding to pF 4) can absorb only moisture from an atmosphere of 99.5% relative humidity. Thus a range of 0.5% relative humidity covers the entire mechanical analysis of soils down to clay, and if it were not for the much smaller particles in the region of ultra-clay we should have almost no moisture absorption from atmospheres of relative humidity less than 99.5%. For the verification of any relation between particle size and moisture absorption at various humidities, the greatest difficulty has been to determine the size distribution of particles smaller than conventional clay. This difficulty has been solved by the micro-pipette technique for the ultra-mechanical analysis of soils described in Part II. Particles of diameters corresponding to pF 5.4 can be experimentally determined.

Still smaller sizes can be determined by extrapolation from the summation curve, assuming that there are none smaller than 10^{-7} cm, corresponding to pF 7, which give interstices of dimensions smaller than water molecules. Between this limiting value and the smallest particle size actually determined, there is admittedly a gap, but the trend of the summation curve is generally smooth enough to leave little doubt as to the actual values to a very close approximation. Thus the following particle sizes were experimentally determined in a number of soils with the micro-pipette: pD 4, pD 4.2, pD 4.6, pD 5.0, pD 5.2, pD 5.4.

TABLE 17. The relation between diameter of particles, the pF of the water held in them and the relative humidity corresponding to that value.

Diameter of particles		Maximum height of water		Relative humidity of capillary water*	Negative pressure in atmospheres
cm	(mm)	cm	pF	%	
10^{-1}	1	10	1		.01
10^{-2}	.1	100	2		.1
10^{-3}	.01	1000	3		1
10^{-4}	.001	10000	4	99.5	10
10^{-5}	.0001	100000	5	92.96	100
10^{-6}	.00001	1000000	6	48.3	1000
10^{-7}	.000001	10000000	7	0.18	10000

*Calculated from the formula $pF = 6.5 + \log_{10} (2-\log_{10} h)$ where h = relative humidity.

The method of calculating mechanical analysis of soils from the vapor pressure-moisture absorption curves may be explained as follows. Knowing the pF value corresponding to particles of various sizes, the relative humidity (h) of the atmosphere required to fill completely the entire pore spaces between such particles can be calculated by the relation

$$pF = 6.5 - \log_{10}(2-\log_{10}h)$$

The amount of moisture absorbed at various humidities (calculated for particles of various sizes) is interpolated from the vapor pressure-moisture absorption curve. If pore space is assumed to be x%, it is evident that with particles of uniform size the percentage moisture absorption of corresponding humidity will be x% also. Suppose actually the moisture absorbed is y%; then the percentage of particles corresponding to this size is $100/x \times y$. In this way the percentage of various particle sizes can be calculated.

The greatest uncertainty about these calculations is the percentage of the pore space. The value may vary between wide limits, depending on whether the packing is closed or open. For soils, 38% pore space is perhaps nearer than any other value. The element of uncertainty remains, however. A more rational and direct approach would be to calculate the pore space in every individual case and not depend on any average value. This is done as follows.

From the pF - pD relationship it is found that particles of conventional clay (0.001 mm diameter) will have their interstices filled from an atmosphere of 99.5% humidity. If we determine the percentage of moisture absorbed by a soil from 99.5% humidity b, and if the percentage of clay is found to be a, then the percentage pore space of the clay fraction of the soil will be $b/a \times 100$. Since this represents the upper limit of the particle size beyond which moisture absorption from the vapor phase cannot take place, we can take this value as the pore space of the clay fraction of the soil. Thus the pore spaces of the various soils in this study are given in Table 18, together with the percentage of clay and moisture absorption at 99.5% humidity.

In order to illustrate the calculations further, data for moisture absorption at various humidities and percentages of particles of various sizes calculated from these data in the case of P.C.2 soils are given in Table 19. Since the clay in this soil as actually determined by the pipette method is 51.8% and moisture absorption at 99.5% humidity is 20.8%, the pore space works out to be 40.1%.

Some important single-value constants for the soils used are given in Table 20. This will emphasize the varied character of the soils, which were of different origin. Results of moisture absorption of various soils from different humidities (interpolated values) corresponding to different particle sizes are given in Table 21. The calculated and observed percentages of particles of various sizes in different soils are given in Table 22.

The remarkable agreement between the calculated and experimentally determined values for a number of soils is more strikingly brought out in Fig. 27, in which the experimentally determined and calculated curves are plotted in the case of some typical soils. Alternatively, of course, the vapor-pressure curve for any soil could be calculated from its ultra-mechanical analysis.

It appears advisable at this stage to guard against a possible misconception that might arise from the supposition that the capillaries corresponding to a particular particle diameter are supposed to be full at the corresponding humidity, and that all the capillaries of larger diameter are empty. This is not strictly correct, as is apparent from the relation between pressure deficiency and moisture content discussed in the last chapter. Actually there is an interval of pressure deficiency equal to $4T/r$, during which the capillary corresponding to radius equal to r is in the process of emptying. We may, therefore, suppose that as the relative humidity

is decreased from one value to another, the moisture saturation of the capillaries must pass through a series of partial fillings. Since in the calculation we assume that the pore space corresponding to a particular diameter is completely full of water, an error is likely to be introduced due to the uncertain cases of capillaries that are partially full.

TABLE 18. Percentage Clay, moisture absorption from 99.5% humidity, and pore space of various soils.

Soil No.	Percentage particles .001 mm (a)	% moisture absorption from 99.5% humidity (b)	Pore space (cc/100 gm soil) = b/a×100
P.C. 2	51.8	20.8	40.15
P.C. 3	57.2	20.9	36.5
P.C. 4	14.6	3.97	27.19
P.C. 5	10.3	3.1	30.1
P.C. 6	25.8	7.7	29.84
P.C. 8	26.2	8.2	31.3
P.C. 9	24.3	9.0	37.0
P.C. 10	37.1	12.0	32.3
P.C. 11	29.6	11.0	37.15
P.C. 12	12.0	6.49	54.08
P.C. 13	54.7	20.5	37.5
P.C. 14	39.8	10.6	26.63
P.C. 16	7.0	3.0	42.85
P.C. 17	15.7	5.4	34.3
P.C. 18	17.7	6.2	35.0
P.C. 19	35.8	12.0	33.5
P.C. 20	6.4	2.4	37.5
P.C. 21	12.0	5.2	43.3
P.C. 22	12.1	4.6	37.7
P.C. 23	10.2	3.5	34.3
P.C. 24	10.8	3.8	35.2
P.C. 26	17.0	6.05	35.6
P.C. 27	46.0	18.6	40.4
P.C. 28	35.2	12.4	35.22
P.C. 29	52.1	19.0	36.5
P.C. 30	48.5	18.0	37.1
P.C. 31	22.0	7.0	31.8
P.C. 32	72.1	30.0	41.6
P.C. 34	9.1	2.7	29.7
P.C. 35	15.2	4.5	29.6
P.C. 36	10.4	2.9	27.9
P.C. 37	7.3	1.9	26.0
P.C. 38	42.2	16.5	39.1
P.C. 39	11.8	3.8	32.2
P.C. 40	12.5	3.65	29.2
P.C. 41	54.5	18.6	34.1
P.C. 42	53.0	20.8	39.2
P.C. 43	20.5	8.8	42.9
P.C. 44	8.1	3.0	37.0
P.C. 45	8.0	3.0	37.5
P.C. 46	51.6	20.2	39.15
P.C. 47	14.1	5.0	35.45
P.C. 48	17.2	6.0	34.9
P.C. 49	25.9	8.0	30.9
P.C. 50	18.6	5.4	29.0
P.C. 51	13.0	4.05	31.15
P.C. 52	10.2	2.75	27.0
P.C. 53	14.0	4.4	31.4
P.C. 54	4.5	1.1	24.44
P.C. 55	12.0	5.45	45.4
P.C. 57	10.3	3.0	29.1
P.C. 59	10.8	3.3	30.55

A moment's reflection, however, would reveal the fact that the magnitude of this error is not likely to be great. As pointed out before, the interval between the emptying of the capillary from a state of saturation is covered by arrange of pressure deficiency of

the order of $(10.5T/r - 6.5T/r) = 4T/r$. This will be equal to a change in the humidity of the order of 1.6% up to particles of 0.0001 mm diameter (pD 5) rising up to about 8% for particles of 0.00001 mm diameter (pD 6). The error is evidently greater in the drier regions, but deviations are systematic and are thus smoothed out on the average. Besides, before one set of capillaries has emptied, others have just started emptying and yet others may be half empty. The net result of this overlapping is that irregularities are smoothed out and simplification of the mathematical treatment is rendered possible.

TABLE 19. Ultra mechanical analysis of soil P.C. 2 calculated from moisture absorption at various humidities.

Particle size cm	pF	Corresponding value for relative humidity	Moisture absorbed % (x)	Percentage of particles $\frac{100\,x}{40.1}$
10^{-4}	4	99.5	20.8	51.8
$10^{-4.2}$	4.2	98.8	19.3	48.2
$10^{-4.6}$	4.6	97.1	19.0	47.3
$10^{-5.0}$	5.0	93.0	17.4	43.1
$10^{-5.2}$	5.2	89.1	16.2	40.3
$10^{-5.4}$	5.4	83.3	15.0	37.4
$10^{-5.6}$	5.6	74.8	13.2	32.9
$10^{-6.0}$	6.0	48.3	9.8	24.5
$10^{-6.2}$	6.2	31.5	8.5	21.2
$10^{-6.5}$	6.5	10.0	5.9	14.7

It may be pointed out that in the case of coarse particles like sands and silts, such a simplification of the treatment would not be possible because the range of particles in the entire sample is so small that no smoothing effect could be expected. Taking an average case, the particles may vary from 0.06 to 0.6 mm diameter. Here is a state of affairs in which, before the pores of particles of 0.6 mm diameter have completely emptied, the partial emptying of the pores of particles of 0.5 mm diameter has already begun; before the latter is complete, the pore space between particles of 0.4 mm diameter has become seriously depleted. It is for this reason that it is not possible to calculate size distribution from the pressure deficiency - moisture content curves of sands, though from their size distribution the entire relation between pressure deficiency and percentage saturation could be obtained (Figure 17).

A close perusal of these results would leave no doubt that moisture absorption, even by particles of ultra-microscopic dimensions, is governed by the same laws of capillarity which operate in macropores in the case of water held by coarse sand against the pull of gravity. The simplicity of this conception should, therefore, re-

place the frequently employed terminology describing the various forms of water such as "imbibitional", "reticular", "colloidal", "adsorbed", "capillary", "hygroscopic", "gravitational", etc. All water in soil is "capillary" water and the so-called differences are merely those due to size of pores and magnitude of free energy.

TABLE 20. Single value constants of P.C. soils.

Soil No.	Exchange Cap.	Exchangeable Base Ca	Exchangeable Base Na	pH
2	81.95*	56.2*	7.35*	8.21
3	91.2	55.8	11.20	7.64
4	20.85	9.0	2.05	9.55
5	19.8	9.1	2.0	8.77
6	27.7	6.3	1.0	5.29
8	37.55	21.2	3.35	8.41
9	25.4	4.2	1.1	5.76
10	44.14	25.5	4.14	8.71
11	44.1	29.2	3.30	8.77
12	19.7	4.4	1.9	5.83
13	74.9	5.56	3.3	8.53
14	41.1	5.6	0.5	5.37
16	15.25	5.8	1.55	8.74
17	19.25	8.6	1.25	8.20
18	25.1	4.0	2.9	5.79
19	43.65	19.0	7.85	8.40
20	14.45	2.3	0.35	5.64
21	25.35	12.1	2.15	8.25
22	27.85	8.5	3.35	6.85
23	22.45	8.4	2.55	7.41
24	-	-	2.55	8.59
26	12.9	6.4	1.6	8.11
27	-	47.2	5.1	9.03
28	50.8	35.2	3.8	8.38
29	68.8	45.6	6.4	8.05
30	71.9	52.6	5.3	8.45
31	-	-	0.6	8.01
32	-	-	-	5.05
34	16.14	5.6	2.2	7.63
35	24.4	9.6	3.4	7.98
36	-	6.1	1.1	8.46
37	-	0.4	-	5.72
38	-	-	-	8.29
39	22.4	8.6	6.0	9.11
40	25.0	8.4	4.0	7.65
41	-	47.6	5.4	8.74
42	-	47.5	8.8	9.00
43	28.2	18.0	1.8	8.41
44	15.9	8.2	1.3	8.54
45	15.4	4.7	2.3	7.45
46	70.8	41.3	7.7	7.63
47	16.5	5.6	5.8	9.98
48	18.1	9.2	2.9	8.55
49	32.2	13.2	4.0	6.33
50	21.8	10.8	2.6	8.54
51	17.4	9.4	2.4	8.68
52	16.5	6.2	2.3	8.02
53	17.5	6.4	5.7	9.87
54	20.5	4.8	6.7	8.71
55	6.6	20.6	1.4	8.36
57	11.2	2.8	8.4	10.40
59	9.6	5.6	4.0	8.86

* All values in m.e./100gm. soil

Within any range, however small, the relation between percentage saturation and free energy or pressure deficiency is perfectly smooth. The total range, however, is vast, extending from micropores of particles of colloidal dimensions to macropores of coarse sands. There are no gaps or breaks within the entire range, but only points of inflection. "Moisture equivalent", "hygroscopic co-

efficient", "hygroscopicity", "wilting coefficient" are arbitrarily chosen single points on the curve. The interrelation between the various points merely indicates that they all lie perhaps on a straight bit of the curve; and since they all refer ultimately to the size of pores, some empirical relation between particle size as

TABLE 21. Results of moisture absorption of various soils from different humidities (interpolated values) corresponding to different particle size (pD).

Soil No. P.C.	99.5 (pD 4)	97.1 (4.6)	92.96 (5.0)	89.08 (5.2)	83.3 (5.4)	74.8 (5.6)	48.3 (6.0)	31.5 (6.2)	10.0 (6.5)	Pore space
2	20.8	19.0	17.33	16.2	15.0	13.2	9.84	8.5	5.9	40.15
3	20.9	19.5	18.2	17.2	15.8	14.0	10.4	8.1	5.8	36.5
4	3.97	3.6	3.1	2.8	2.4	2.0	1.3	1.2	0.8	27.19
5	3.1	2.7	2.4	2.0	1.7	1.5	0.85	0.7	0.6	30.1
6	7.7	7.1	6.4	5.8	4.8	3.3	1.75	1.45	1.06	29.84
8	8.2	7.0	6.0	5.6	5.3	4.9	3.3	2.65	1.75	31.3
9	9.0	7.6	6.0	4.8	3.8	2.8	1.4	1.15	0.72	37.0
10	12.0	10.2	9.2	8.7	8.0	6.85	4.5	3.5	2.70	32.3
11	11.0	9.8	8.6	8.0	7.4	6.80	4.6	3.85	2.70	37.15
12	6.49	3.0	2.2	1.9	1.4	1.1	0.4	0.3	0.22	54.08
13	20.5	17.6	16.0	15.1	13.8	12.4	9.18	7.6	4.8	37.5
14	10.6	9.0	7.5	6.6	5.2	3.5	1.98	1.25	0.35	26.63
16	3.0	2.0	1.4	1.2	1.0	0.7	0.4	0.3	0.07	42.85
17	5.4	3.8	3.1	2.5	2.0	1.5	0.8	0.55	0.10	34.4
18	6.2	5.4	4.6	3.8	3.0	2.3	1.5	1.2	0.57	35.0
19	12.0	9.6	8.4	8.0	7.1	6.15	4.25	3.2	1.65	33.5
20	2.4	1.6	1.05	0.8	0.6	0.58	0.3	0.25	0.18	37.5
21	5.2	4.0	3.4	3.0	2.5	2.10	1.4	1.15	0.58	43.3
22	4.6	3.8	3.2	2.9	2.6	2.2	1.5	1.35	0.94	37.7
23	3.5	2.8	2.2	2.0	1.7	1.6	1.1	0.9	0.5	34.3
24	3.8	3.4	2.8	2.4	1.9	1.3	0.8	0.65	0.26	35.2
26	6.05	5.05	4.7	4.5	4.1	3.7	0.8	0.6	0.2	35.6
27	18.6	14.6	13.3	12.7	11.8	10.9	8.3	6.4	3.5	40.4
28	12.4	10.2	9.3	8.7	8.0	7.1	5.25	4.1	2.2	35.22
29	19.0	15.7	14.7	13.8	12.65	11.3	8.00	6.0	3.6	36.5
30	18.0	17.1	15.8	14.8	13.5	12.3	9.6	7.4	4.38	37.1
31	7.0	6.1	5.5	5.05	4.6	3.8	2.7	2.1	1.14	31.8
32	30.0	21.8	18.0	16.0	14.0	12.0	6.5	5.0	2.58	41.6
34	2.7	2.3	1.95	1.75	1.5	1.2	0.85	0.7	0.38	29.7
35	4.5	4.0	3.6	3.3	2.95	2.6	1.8	1.5	0.83	29.6
36	2.9	2.55	2.2	1.95	1.70	1.5	0.8	0.5	0.38	27.9
37	1.9	1.5	1.2	1.1	0.95	0.85	0.55	0.4	0.32	26.0
38	16.5	14.8	13.9	13.1	12.1	10.8	7.7	6.2	3.91	39.1
39	3.8	3.4	3.05	2.75	2.5	2.2	1.4	1.05	0.59	32.2
40	3.65	3.35	3.05	2.8	2.5	2.4	1.6	1.3	0.76	29.2
41	18.6	17.0	15.7	14.9	13.7	12.4	9.4	7.6	4.56	34.1
42	20.8	18.6	16.8	15.6	14.2	12.8	9.1	7.1	4.2	39.2
43	8.8	6.0	5.2	4.8	4.2	3.5	2.2	1.7	1.0	42.9
44	3.0	2.4	2.0	1.8	1.55	1.2	0.8	0.75	0.68	37.0
45	3.0	2.4	2.0	1.8	1.55	1.2	0.6	0.50	0.27	37.5
46	20.2	17.6	16.3	15.4	14.0	12.3	8.8	7.1	4.36	39.15
47	5.0	3.9	3.3	2.8	2.3	1.6	0.9	0.65	0.29	35.45
48	6.0	4.8	4.2	3.6	2.9	2.0	1.05	0.80	0.54	34.9
49	8.0	6.8	6.1	5.6	5.0	9.1	2.1	1.40	0.56	30.9
50	5.4	4.3	3.8	3.4	2.8	2.0	0.9	0.40	0.05	29.0
51	4.05	3.3	2.7	2.3	1.9	1.5	0.5	0.15	0.000	31.15
52	2.75	2.3	1.9	1.7	1.4	1.15	0.3	0.1	0.00	27.0
53	4.4	3.9	3.4	2.95	2.4	1.85	1.15	0.9	0.6	31.4
54	1.1	0.9	0.8	0.8	0.7	0.45	0.35	0.3	0.22	24.44
55	5.45	4.4	3.8	3.35	2.8	2.0	1.15	0.9	0.53	4.54
57	3.0	2.45	2.05	1.85	1.55	1.15	0.70	0.5	0.39	29.1
59	3.3	3.0	2.55	2.2	1.95	1.70	1.38	1.05	0.59	30.55

representedby mechanical analysis and moisture equilibrium points is not at all difficult to conceive.

The rate of moisture absorption from the vapor phase is governed by pressure gradient. We have seen that the maximum diameter of interstices between particles of conventional clay (0.001 mm) is such that water can condense in them from the vapor phase

only if the relative humidity is higher than 99.5%. Hence even from an atmosphere 100% saturated, the pressure gradient will be so low that any moisture equilibrium within measurable time would be impossible. Conventional clay, therefore, does mark to some extent the limit of moisture absorption through the vapor phase, and the old empirical relation between hygroscopic coefficient and clay

TABLE 22. Calculated and observed values of mechanical analysis of soils.

Soil No.	Diameter							
	pD→ 4.0 mm→ 0.001	4.2 0.0006	5.0 0.0001	5.2 0.00006	5.4 0.00004	6.0 0.00001	6.2 0.000006	6.5 0.000003
2	F 51.8	49.4	42.6	30.6	27.4	17.0	13.5	8.2
	C 51.8	48.16	43.15	40.34	37.36	24.5	21.17	14.70
3	F 57.2	55.6	50.0	37.5	35.5	22.8	18.8	12.0
	C 57.2	56.43	49.86	47.11	43.25	28.49	22.19	15.89
4	F 14.6	8.9	4.9	3.5	2.8	1.7	1.2	1.0
	C 14.6	13.61	11.40	10.3	8.83	4.78	4.41	2.94
5	F 10.3	8.3	4.8	4.0	2.8	1.8	1.4	1.0
	C 10.3	9.63	7.97	6.64	5.65	2.82	2.33	1.99
6	F 25.8	24.0	16.9	15.2	13.5	8.16	6.2	3.8
	C 25.8	25.14	21.45	16.44	16.09	5.87	4.86	3.55
8	F 26.2	23.9	21.0	19.2	18.0	12.2	10.1	6.2
	C 26.2	25.24	19.17	17.90	16.94	10.54	8.47	5.59
9	F 24.3	24.1	14.7	8.4	7.7	3.32	2.5	1.4
	C 24.3	23.52	16.22	12.98	10.27	3.78	3.11	1.95
10	F 37.1	34.3	28.0	25.0	20.2	12.5	10.0	6.5
	C 37.1	35.77	28.5	26.93	24.78	13.94	10.84	8.36
11	F 29.6	27.2	24.0	23.8	20.5	13.0	10.2	6.5
	C 29.6	28.0	23.15	21.54	19.93	12.39	10.37	7.27
12	F 12.0	10.1	6.1	4.7	4.0	2.5	2.0	1.2
	C 12.0	7.03	4.07	3.51	2.59	2.74	2.55	2.41
13	F 54.7	49.9	41.0	34.7	30.2	18.3	14.5	9.0
	C 54.7	49.07	42.67	40.26	36.8	24.48	20.27	12.8
14	F 39.8	35.0	19.1	17.0	16.3	9.0	7.1	4.5
	C 39.8	37.93	28.16	24.79	19.53	7.44	4.69	1.31
16	F 7.0	7.0	2.5	2.0	1.6	1.0	0.9	0.3
	C 7.0	5.35	3.27	2.80	2.33	0.93	0.7	0.16
17	F 15.7	11.3	7.8	7.0	4.9	3.0	2.5	2.0
	C 15.7	13.37	9.01	7.27	5.81	2.33	1.60	0.29
18	F 17.7	17.5	11.8	8.04	4.1	2.3	1.5	1.2
	C 17.7	16.0	13.15	10.86	8.57	4.29	3.43	1.63
19	F 35.8	32.0	23.8	21.4	15.6	10.3	8.4	5.0
	C 35.8	31.65	25.08	23.88	21.2	12.69	0.55	4.92
20	F 6.4	6.0	4.5	3.8	3.0	1.5	1.0	2.7
	C 6.4	5.87	2.80	2.13	1.60	0.80	0.67	0.48
21	F 12.0	9.9	5.5	4.5	3.6	2.0	2.0	1.5
	C 12.0	11.09	7.39	6.93	5.73	3.23	2.65	1.34
22	F 12.2	11.0	7.4	5.5	3.9	2.2	1.5	1.3
	C 12.2	11.67	8.49	7.69	6.90	3.98	3.58	2.49

TABLE 22. (Continued)

	Diameter							
Soil	pD→ 4.0	4.2	5.0	5.2	5.4	6.0	6.2	6.5
No.	mm→ 0.001	0.0006	0.0001	0.00006	0.00004	0.00001	0.000006	0.000003
23	F 10.2	9.5	5.1	4.6	3.5	1.5	1.1	0.6
	C 10.2	9.91	6.41	5.83	4.96	3.21	2.62	1.46
24	F 10.8	10.1	7.2	6.5	4.9	3.2	2.8	1.8
	C 10.8	10.51	7.95	6.92	5.40	2.27	1.85	0.74
26	F 17.0	16.1	10.8	8.5	5.1	3.5	2.6	1.0
	C 17.0	16.58	13.2	12.64	11.52	2.25	1.68	0.56
27	F 46.0	44.2	39.0	33.5	26.1	16.0	12.2	7.1
	C 46.0	43.57	32.92	31.44	29.2	20.54	15.84	8.66
28	F 35.2	34.9	22.0	19.2	16.2	9.0	7.0	4.1
	C 35.2	33.78	26.4	24.7	22.72	14.91	11.64	6.25
29	F 52.1	50.7	38.0	31.6	28.5	17.4	13.8	8.1
	C 52.1	50.41	40.27	37.8	34.66	21.92	16.44	9.86
30	F 48.5	45.7	35.6	29.8	27.2	17.0	13.6	8.5
	C 48.5	47.98	42.58	39.89	36.39	25.88	19.95	11.81
31	F 22.0	20.5	18.2	13.2	11.4	6.5	5.2	3.3
	C 22.0	21.38	17.30	15.88	14.47	8.49	6.60	3.58
32	F 72.1	67.6	41.5	37.9	30.1	18.7	15.2	9.8
	C 72.1	63.95	43.27	38.46	33.65	15.63	12.02	6.20
34	F 9.1	6.8	4.2	3.1	1.9	1.0	0.9	0.4
	C 9.1	8.78	6.57	5.89	5.05	2.86	2.36	1.28
35	F 15.2	12.9	8.5	8.0	5.5	3.2	2.7	1.8
	C 15.2	14.87	12.16	11.15	10.07	6.08	5.07	2.80
36	F 10.4	7.8	4.3	3.5	2.0	1.0	0.9	0.4
	C 10.4	10.04	7.89	6.99	6.09	2.87	1.79	1.36
37	F 7.3	4.0	2.7	2.4	1.2	0.8	0.6	0.4
	C 7.3	6.92	4.61	4.23	3.65	2.11	1.54	1.23
38	F 42.2	43.9	34.8	29.6	23.5	14.2	11.5	7.4
	C 42.0	41.44	35.55	33.5	30.95	19.7	15.86	10.0
39	F 11.8	11.5	7.8	5.1	4.0	1.6	1.3	0.8
	C 11.8	11.5	9.47	8.53	7.76	4.35	3.26	1.83
40	F 12.5	11.0	9.0	6.8	4.6	2.7	2.0	1.3
	C 12.5	11.99	10.45	9.59	8.56	5.48	4.45	2.06
41	F 54.5	48.2	36.4	32.7	28.4	17.5	14.2	8.8
	C 54.5	53.96	46.04	43.7	40.17	27.57	22.29	13.37
42	F 53.0	48.5	35.4	28.8	27.0	16.5	13.0	8.2
	C 53.0	52.3	42.86	39.8	38.22	23.22	18.11	10.74
43	F 20.5	16.8	7.4	5.9	4.2	2.5	2.1	1.2
	C 20.5	19.57	12.12	11.19	9.79	5.13	3.96	2.33
44	F 8.1	7.0	3.2	2.9	2.0	1.0	0.8	0.4
	C 8.1	7.57	5.40	4.86	4.19	2.16	2.03	1.84
45	F 8.0	7.2	5.6	5.0	2.3	0.8	0.6	0.4
	C 8.0	7.47	5.33	4.80	4.13	1.60	1.33	0.72
46	F 51.6	47.4	37.5	31.6	28.4	18.0	14.5	9.0
	C 51.6	50.3	41.64	39.34	35.77	22.48	18.14	11.14
47	F 14.1	11.6	6.4	4.5	3.5	2.0	1.8	1.2
	C 14.1	13.54	9.31	7.90	6.49	2.54	1.83	.82
48	F 17.2	13.2	7.2	6.5	4.0	2.5	2.0	1.2
	C 17.2	16.33	12.03	10.31	8.31	3.01	2.20	1.55

TABLE 22. (Continued)

Soil No.	Diameter: pD→ 4.0 mm→ 0.001	4.2 0.0006	5.0 0.0001	5.2 0.00006	5.4 0.00004	6.0 0.00001	6.2 0.000006	6.5 0.000003
49	F 25.9	22.2	17.8	10.5	8.4	5.6	4.5	3.0
	C 25.9	24.6	19.42	18.13	16.18	6.80	4.53	1.81
50	F 18.6	13.1	7.0	6.0	3.5	2.0	1.0	0.5
	C 18.6	17.59	13.10	11.72	9.65	3.10	1.38	0.17
51	F 13.0	11.2	3.0	2.4	1.6	0.8	0.6	0.4
	C 13.0	12.52	8.67	7.39	6.10	1.60	0.48	0
52	F 10.2	9.0	7.0	6.4	4.7	2.7	2.0	1.3
	C 10.2	9.63	7.04	6.30	5.18	1.11	0.37	0
53	F 14.0	12.5	5.6	4.4	3.0	1.5	1.2	1.0
	C 14.0	13.38	10.83	9.40	7.64	3.66	2.87	1.91
54	F 4.5	3.8	2.5	2.2	1.4	0.8	0.6	0.3
	C 4.5	4.30	3.27	3.27	2.86	1.43	1.23	0.90
55	F 12.0	10.4	6.0	4.8	3.6	2.1	1.8	1.2
	C 12.0	11.45	8.37	7.38	6.17	2.53	1.98	1.17
57	F 10.3	8.0	3.0	1.6	1.4	0.8	0.6	0.4
	C 10.3	9.62	7.04	6.36	5.33	2.40	1.72	1.34
59	F 10.8	8.2	5.6	4.9	4.2	3.0	2.5	1.7
	C 10.8	10.51	8.35	7.20	6.38	4.52	3.44	1.93

F = Determined
C = Calculated

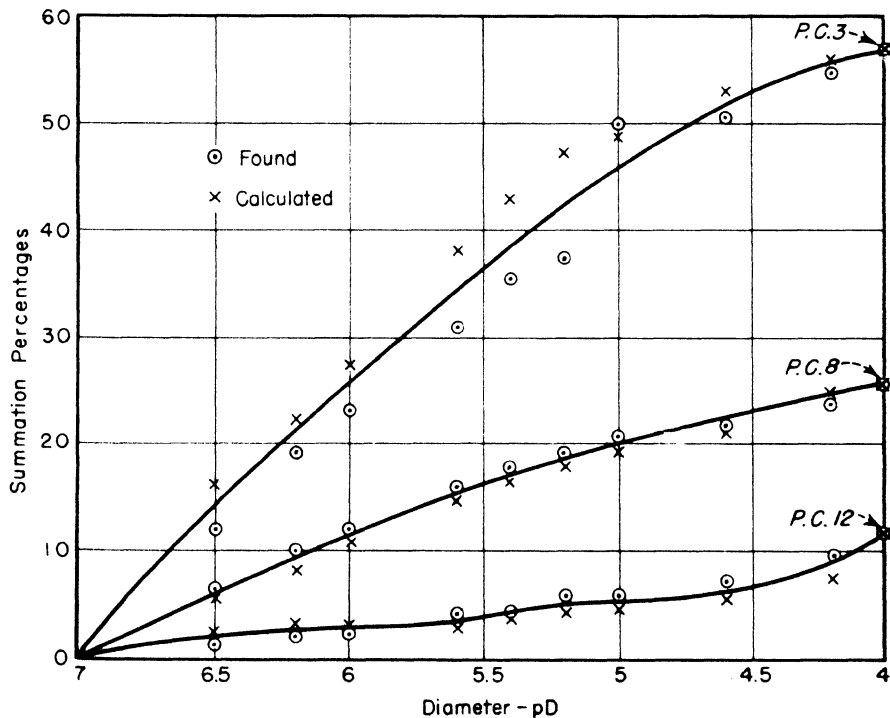



Fig. 27. Calculated and Determined Values of Ultra-clay Fractions of Soils

content can thus be understood. The pressure gradient in this region, however, is so low that any attempt at exactitude would be futile.

It must be remembered that the absorption of moisture in this region is on the rising curve of the hysteresis loop and must fall considerably short of the equilibrium value attained by the withdrawal of water. The latter values may be more reliable since they make use of the application of pressure deficiency through suction which can be controlled with greater precision. The advantages of Briggs and MacLean's "moisture equivalent" or Bouyoucos' "suction equivalent" are obvious, in spite of the fact that their fundamental value is still doubtful. There is also no reason why such values can not be replaced by pressure deficiency-percentage saturation curves based on the aggregate analysis of the soils, with the help of some such capillarimeter as described in the foregoing. Just as the pH value of a soil has no more significance than that it is a single point on its titration curve; just as the clay or silt content of a soil has no more significance than that they are arbitrarily fixed points on the size distribution curve - similarly moisture content of a soil determined under any prescribed set of conditions has no more significance than that it is some point on its vapor pressure curve. A great deal of confusion is due to failure to recognize this fact.

Considerable controversy in soil literature has raged around the much debated question as to how high water can rise in the soil. We have seen that in sands not only can we calculate and experimentally verify how high moisture will rise, but also determine the moisture distribution throughout the entire height. If the sand column is flooded with a limited quantity of water we can calculate from the geometry of the interstitial spaces how far the water will go. If on the other hand free drainage is provided, we can compute the moisture distribution from the falling curve of the hysteresis loop of the capillary curves.

The presence of clay in the soil introduces complications which restrict the movement of moisture by reducing the pore size; moreover, by holding a good deal of water in the micropores, clay renders the application of pressure deficiency inoperative beyond a certain limit. For practical purposes of moisture distribution in the field, the water held in the micropores can be considered a common factor at all stages. It is the aggregate mechanical analysis that determines the moisture distribution in such cases, as well as the maximum height to which the water can rise.

It is obvious, however, that there is no limit to the movement of moisture in the vapor phase to any height, provided the micropores are small enough to establish the vapor pressure gradient. The movement of water in mass, however, must be restricted by the size of macropores. In actual practice under field conditions we are concerned only with moisture in the macropores, the lower

limit of which is formed by particles of the size corresponding to conventional clay having a free energy equal to pF 4. This also marks the lower limit of moisture, known as wilting coefficient, which is the moisture content below which plants cannot withdraw water from the soil for their use.

The fact that the wilting coefficient of soils is of the order of pF 4.2 is likely to give an erroneous idea of the mechanism of moisture absorption by root hairs. For instance, it would seem that the limiting factor is the suction pressure of the soil, and a possible connection between the suction pressure of the roots and that of the soil might be sought. A moment's reflection will show that this idea is likely to be misleading. The limiting factor in the utilization of soil moisture may not be the suction pressure but the limiting size of the root hairs, which cannot penetrate capillaries below a certain diameter.

The development of suction pressure in soils is entirely due to surface tension, and unless a root hair can enter and establish contact with the water surface the plant cannot take up moisture. This condition of isolation evidently begins to operate when the moisture has receded to the capillaries formed by particles of 0.0001 cm diameter, corresponding to pF 4.

The importance of the clay fraction in determining wilting coefficient is at once apparent. Since clay represents only the upper limit of particles of this size, the exact relation must depend on the size distribution of finer particles in the clay fraction. Particles coarser than clay are mainly responsible for retaining moisture that is available to plants; clay merely helps in the conservation of this moisture by preventing evaporation and maintaining soil air at high humidity.

It might be pointed out that in working out the relation between maximum capillary pull as determined by the capillarimeter and the mean diameter in the case of soils, the lowest limit of size for calculating the mean diameter is taken as 0.0001 cm, in spite of the fact that there is a large percentage of finer particles which, if included, would reduce the mean diameter considerably. The main contention that emerges from these considerations is that there is a limit to the continuity of the liquid phase when pressure deficiency or suction force is applied to soils. When this force exceeds that required to empty capillaries formed by particles coarser than clay, gaps are created through which transmission of suction pressure cannot take place.

If a wet soil is placed on a dry soil, the suction created by the latter cannot be transmitted when the moisture has been reduced to pF 3.3 (field moisture). Although centrifugal force is not limited by similar considerations and it is theoretically possible to reduce the moisture content to any value down to dryness, there are practical difficulties in the production of such an enormous force, and we are again limited to a pF value of 3 (moisture equivalent). Plants,

on the other hand, through their minute root hairs, can reach much smaller capillaries; but it must be emphasized that the limiting factor may not be the suction pressure of the roots but the size of the capillaries. It is for this reason that the wilting coefficient must be regarded as a soil characteristic which bears no relation to the suction force of the roots. In fact, it is doubtful whether the magnitude of the suction force of roots plays any part in determining the limiting value of water intake from soils.

In considering the rise and distribution of water in a dry soil through capillarity, a fundamental mistake is made in laying too much emphasis on the vertical height from the free water surface. The whole idea of Buckingham's capillary potential is based on the erroneous assumption that the height of the capillary front is the limiting factor. As a matter of fact, the capillary movement is uninfluenced by gravity, and is the same in all directions. In order to visualize the mechanism of the rise of moisture in a dry soil, we must remember that this movement can take place only from larger to smaller capillaries. In other words, a dry soil will withdraw moisture from a wet soil only if the former contains some capillaries smaller than the largest ones in the latter which may be full of water. Each layer of dry soil therefore draws water from the wet layer next to it, and the mean diameter of capillaries responsible for this pull becomes smaller and smaller as the distance from the free water increases, until the capillaries required for exerting the pull are so small that they are unable to establish contact, and the visible movement stops.

We have thus a sharp line dividing the wet and the dry soil. The total height of the capillary moisture attained in this way bears no relation to the suction force of the soil except qualitatively. It is, however, related to the size distribution of particles, which determine the size of capillaries and the moisture gradient attained. When we speak of the abrupt stoppage of moisture movement in a vertical column of soil we refer only to the wetness visible as a change in the color of the soil. It must not be inferred, however, that there is no movement of moisture beyond this point. Actually there is, but it is confined to capillaries which are too small to show their wetness. As a matter of fact, this movement is very important in connection with the movement of salts in soils. It can be shown that salts move with water even when the moisture content of the soil corresponds to a relative humidity of 75 per cent or pF 5.6. This movement can be stopped, however, by interposing a layer of sand, the capillaries of which may be too large to draw out water from the finer capillaries in the soil. This principle has been successfully used in preventing salt efflorescence on earth roads in salt areas.

The experimental verification of the size distribution of particles calculated from moisture absorption at various humidities throws much light on the mechanism of moisture absorption not only by

soils, but by all capillary systems, such as activated charcoal, silica and alumina. The general similarity of vapor pressure curves for these substances will be shown later.

There is no reason to suppose that the mechanism should be in any way different from that of soils. The existence of minute cells in plant materials is well known, and it is no strain on the imagination to suppose that the driving away of volatile matter from wood leaves behind the framework of carbon residue presenting a cellular structure. It is true that in this case we have yet no means of separating the individual particles forming the cellular structure as in the case of soils, and thus verify the theoretical deductions experimentally; but the general similarity of the curves should leave no doubt that the mechanism of moisture absorption is the same in both cases. These results also place in our hands a powerful method of determining the size distribution of capillaries in porous substances or the ultra-mechanical analysis of capillary systems the particles of which could not be directly determined by dispersion.

CHAPTER VI

REPLACEMENT OF AIR IN THE WATER-AIR INTERFACE BY ORGANIC LIQUIDS AND ITS EFFECT ON VAPOR PRESSURE OF CAPILLARY SYSTEMS

The relation between the vapor pressure at a plane and a curved surface is expressed by the following thermodynamic equation:

$$\log \frac{p'}{p} = \frac{2T}{r\rho} \quad \frac{1}{R\theta}$$

where p = vapor pressure at a plane surface.
p' = vapor pressure at a curved surface.
r = radius of the capillary.
ρ = density of the liquid.
T = surface tension of the liquid.
θ = absolute temperature.
R = the gas constant.

For moisture held in the soil for any fixed size of capillaries corresponding to a relative humidity (h) we can write:

$$\log h = KT$$

If by the replacement of the air in the water-air interface by an organic liquid having an interfacial tension of T', the relative humidity changes thereby to h', and we have:

$$\log h' = \frac{T'}{T} \log h$$

or

$$h' = (h)^{T'/T}$$

Thus if we could measure h we could test this relationship which, if found correct, would afford strong evidence in favor of the contention that water in the soil is held in micropores by surface tension forces and that the well-known laws of capillarity are equally applicable to micropores down almost to molecular dimensions.

For the measurement of the vapor pressure of salt hydrates, several investigators have used distribution methods, combined with some physical method of measurement for determining the concentration of water in the liquid phase. Wilson and Noyes and Westerbrook brought salt hydrates into equilibrium with amyl alcohol and determined the concentration of dissolved water by colorimeteric comparison with cobalt chloride solutions, or by the conductivity of the solutions after the addition of excess potassium thiocyanate. The water concentration at equilibrium was not proportional to the vapor pressure, since the solutions obtained were not sufficiently dilute to be regarded as of constant thermodynamic environment.

Sidgwick showed that the freezing point of benzene is depressed by 0.100°C by saturation with water, and that the efficiencies of the solid drying agents normally used in the organic chemistry laboratory could be ascertained by the freezing point depression (F.P.D.) of the benzene in equilibrium with them. The measurement of vapor pressure by the F.P.D. of benzene in equilibrium with the substance in question has the advantage that the slight solubility of water in benzene (0.03%) results in the transference of very small amounts of water, and renders possible its application to small quantities of materials of low water content. The method was successfully used by the author in collaboration with Crowther in the case of soils, and the validity of the relation $h' = (h)^{T'/T}$ was thus proved. The following detailed account is taken from the paper referred to.

The validity of the assumption that dissolved water in benzene behaves as an ideal solution, and that the concentration of water as measured by the F.P.D. is proportional to the relative vapor-pressure of the added substance, is established by the experiments on sulphuric acid-water mixtures described below.

The sample of benzene was recrystallized several times until the freezing point of the dried sample was constant. This recrystallization was found necessary because the earlier samples showed a steady rise in freezing point if kept frozen for some time, due apparently to the escape of some volatile impurity. The measurements of the F.P.D. were made with the usual Beckmann technique, the cooling chamber being kept at 2-3°C by lumps of ice floating in a large quantity of water, which was kept well stirred in a heavily lagged bath. For each determination 50 cc of benzene was taken from a stock bottle containing metallic sodium, and before each series, measurements were made on two samples, treated respectively with water and phosphorus pentoxide. In all cases the differences in freezing points were 0.100 ± 0.001°C, as recorded by Sidgwick. The tube was open to the air only through the narrow glass tube through which the stirrer passed. There was, therefore, some possibility of traces of water being picked up from the air, but no appreciable error was introduced in this way, since mea-

surements were made in every case in the presence of an excess of a material whose vapor pressure would not be changed perceptibly by such small amounts of water.

Preliminary experiments with varied amounts of sulphuric acid-water mixtures showed that 4 cc of the mixture was sufficient to give constant results. After each reading the benzene was melted and well stirred, and the process repeated several times. With sulphuric acid-water mixtures there was occasionally a change of 0.002°C between the first and second reading, and no subsequent change in some dozen readings. To test the possibility of any interaction between the sulphuric acid and benzene, especially with the more concentrated acids, samples were left overnight in contact with the benzene, and in no case was any change in F.P.D. found. Whereas the sulphuric acid-water mixtures rapidly came to equilibrium with the benzene, soils gave constant readings only after several repetitions of the freezing and melting. Successive readings of the freezing point increased by 0.004 to 0.001°C for the first three or four repetitions, and then became steady. All the results quoted are the averages of some successive 6 to 10 readings, which did not vary by more than 0.002°C.

The F.P.D. resulting from the addition of successive lots of 2 grams of soil in 50 cc of benzene showed that no further change took place after the addition of 10 grams of soil, and that the F.P.D. was the same for either dry or wet samples of benzene. Ten grams of soil were used for all the subsequent experiments. At the end of each series of readings water was added in excess and the freezing point thus obtained was in every case identical with that of the original wet sample of benzene. This is definite proof that nothing was dissolved from the soil by benzene. Since F.P.D. of 0.1°C corresponds to 100% humidity, the calculated relative humidity of any substance in equilibrium with benzene is taken as F.P.D. x 1000. This is true of sulphuric acid-water mixtures and salt hydrates. For soils the vapor pressure of which is altered by the introduction of a benzene-water interface the true relative humidity is equal to

$$(\text{F.P.D.} \times 1000)\ 0.478; \quad T'/T = 35.8/75.0 = 0.478$$

Four soils belonging to widely different types were brought to definite humidities by keeping them over sulphuric acid-water mixtures of known strength. The known relative vapor pressures in the case of sulphuric acid-water mixtures as well as soils were compared with the calculated values from F.P.D. of benzene. The results are given in Table 22A.

The agreement between the calculated and known values of relative vapor pressures is very close and well within the experimental error of the determinations, thus proving the contention that all water held in the soils exists as capillary condensed water in the micropores formed by closely packed discrete particles.

The freezing-point method is of limited application and can be used only with liquids having their freezing points within a convenient range of measurement. The estimation of moisture in benzene

TABLE 22A. Relative vapor pressures of H_2SO_4 - water mixtures and soils calculated from F.P.D. compared with known values.

H_2SO_4 - water mixtures
Relative vapor pressure = F.P.D. x 1000

Relative vapor pressure (Known)	F.P.D. (Observed)	Relative vapor pressure Calculated
97.7	0.098	98
88.5	0.090	90
70.2	0.070	70
41.6	0.041	41
19.5	0.019	19
9.5	0.009	9
1.5	0.001	1

Soils

Calculated relative vapor pressure = $(\text{F.P.D.} \times 1000)^{0.478}$

Relative vapor pressure (Known)	F.P.D. (Observed)	Relative vapor pressure (Calculated)	Moisture content (%)
	Harpenden Common soil		
2	0.009	0.65	0.035
10	0.030	9.57	0.81
30.5	0.058	31.26	1.54
46	0.069	46.03	2.13
59	0.080	62.70	2.66
74	0.090	80.17	3.40
	Woburn soil		
88.5	0.100	100.0	1.88
70.2	0.080	62.7	1.25
41.6	0.070	47.42	0.91
19.5	0.045	18.81	0.60
9.5	0.035	11.12	0.41
1.5	0.018	2.76	0.06
	Rothamsted soil		
88.5	0.100	100.0	3.98
70.2	0.083	62.72	2.88
41.6	0.069	46.03	2.05
19.5	0.049	22.40	1.17
9.5	0.039	13.96	0.87
1.5	0.009	0.65	0.30
	Sudan clay soil		
88.5	0.100	100.0	13.34
70.2	-	-	10.57
41.6	0.064	39.36	8.25
19.5	0.047	20.61	5.46
9.5	0.031	8.63	3.94
1.5	0.018	2.76	1.14

and other organic liquids by some direct method would greatly facilitate verification of the surface-tension effects in the case of other liquids. One such method is the estimation of moisture in the organic liquid, by allowing it to react with sodium metal and measuring the volume of hydrogen evolved. Obviously this method

would be capable of extreme sensitivity. Confirmatory experiments were first taken up with benzene in order to standardize the working conditions, and to verify the results already obtained with the liquid. Toluene and xylene were the other liquids tried. All these were obtained in the pure dry condition by first keeping them overnight in contact with fused calcium chloride and then distilled once. Benzene was then redistilled over sodium wire, while toluene and xylene were first kept overnight with sufficient quantity of anhydrous copper sulphate and then redistilled. All the liquids were then kept well protected from atmospheric moisture and in contact with sodium wire in the stock bottle, from which a portion was taken for test whenever required.

In order to increase the surface of sodium metal to facilitate the decomposition of water held in the organic liquid, it was converted into small beads by melting under xylene in a round-bottomed flask and shaking vigorously after closing the mouth with a rubber bung. Xylene was then replaced by a small volume of the dry organic liquid under test, the beads being kept under that liquid until required.

Dry organic liquid kept with sodium wire was shaken with H_2SO_4-water mixtures for one hour to study the relation between the vapor pressure and the amount of dissolved water.

The arrangement of apparatus for studying the reaction of moist organic liquids with sodium beads is shown in Figure 28. Carbon dioxide is evolved in a hard glass tube by heating sodium bicarbonate and, after drying completely over fused $CaCl_2$ and then H_2SO_4, is passed through the reaction vessel having threeway openings. The CO_2, after passing through the reaction vessel containing sodium beads under a thin layer of dry benzene or the organic liquid under test, is led on through a condenser to a nitrometer burette tube containing KOH solution. The reaction vessel is kept immersed in a water bath at 70°C, and CO_2 is passed for some time before the introduction of the wet sample under test. Through the third opening in the reaction vessel, 50 cc of organic liquid, the moisture content of which is to be determined, is dropped in after all the air has been replaced by CO_2. The reaction vessel is kept heated to a temperature of about 70°C and any organic liquid evaporated is returned to the vessel after being cooled in the condenser. The hydrogen evolved is swept into the nitrometer with a gentle stream of CO_2, and when the reaction is complete its volume is measured and reduced to N.T.P., from which the amount of water in the benzene or the organic liquid under test is calculated.

The relation between the amount of water in benzene (or any other organic liquid used for the purpose) as calculated from the H evolved in every case and the relative vapor pressure of the H_2SO_4- water mixture with which it is in equilibrium is plotted, and from this intermediate values can be interpolated.

The success of the method of determining moisture in organic

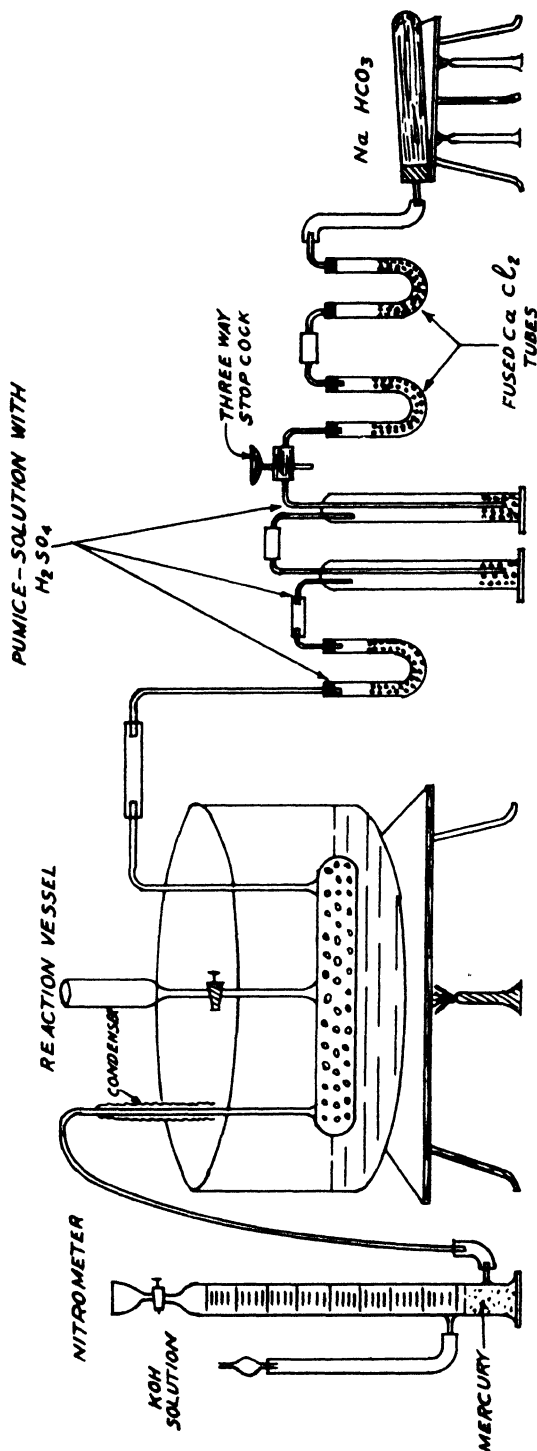



Fig. 28. Diagram of Apparatus for Finding Moisture in Organic Liquids

liquids described in the foregoing obviously depends on the removal of all traces of moisture from the apparatus. This is by no means an easy matter and the technique was mastered only after a number of trials and failures. A simpler method was also tried with success, partly to simplify the technique and partly to collect corroborative evidence by two independent methods.

The method consists in absorbing the moisture in the organic liquid over anhydrous copper sulphate and weighing it. Fifty cc of the liquid is slowly percolated through a weighed quantity of anhydrous copper sulphate held in a Gooch crucible. If a liquid like toluene or xylene is used, then subsequent washing with pure dry ether is essential. The crucible is then dried in an air-oven maintained at a temperature of 70 to 80°C, whereupon all the organic liquid is evaporated, but the water is held back. After drying, the crucible is cooled in a desiccator containing freshly ignited $CaCl_2$ for about 10 minutes, and then weighed.

To prevent any atmospheric moisture from getting in, the crucible is closed with a cork having a bore in which the pipette containing the organic liquid is inserted. The pipette at the top is closed with a rubber tube and pinchcock to regulate the flow of the liquid. The suction, applied through the filter pump, is also light, so that the liquid may percolate through, drop by drop. This insures complete absorption of the moisture in the organic liquid by the anhydrous copper sulphate.

The results obtained by shaking benzene, toluene and xylene with H_2SO_4-water mixtures of varying humidity at 40°C are given in Tables 23 and 24. In the case of benzene the results with both methods are given, triplicate determinations being made in the case of the $CuSO_4$ method. In case of toluene and xylene, only the first method, *i.e.*, the hydrogen-displacement method was used. After equilibrium has been attained (1 hour) the supernatent layer was pipetted off and the moisture in the organic liquid determined either by the H displacement or the $CuSO_4$ method.

The results in Tables 23 and 24 are plotted in Figures 29 and 30. These constitute the basic curves from which the water content of the three liquids could be determined from the relative humidity of the moist substance with which they may be in equilibrium.

Three soils and a sample of silica were brought into equilibrium with atmospheres of varying humidity. The equilibrium moisture contents of the samples varied a great deal, as will be seen from Table 25. Ten grams of the moist soil or silica were shaken with 70 cc of the organic liquid for 1 hour at 40°C. Fifty cc of the organic liquid were pipetted off and the water content determined by the H displacement or $CuSO_4$ method. From the known humidity with which the soil was in equilibrium the relative humidity assumed by it on account of the replacement of the air-water interface by organic liquid-water interface was calculated from the formula previously given. The water content of the organic liquid

corresponding to this calculated relative humidity was interpolated from the curves in Figures 29 and 30. These calculated values along with those actually determined are given in Table 26.

The agreement between the calculated and determined values in

TABLE 23. Water content of benzene in equilibrium with H_2SO_4 - water mixtures at 40° C.

Relative Humidity (%)	Mgm. water in 50 cc of benzene			
	CuSO4 method			H displacement method
	(a)	(b)	(c)	
10	9.0	10.0	10.0	6.0
30	13.5	14.0	13.5	11.36
50	17.0	15.5	16.5	16.6
70	20.5	21.0	21.5	22.32
90	25.5	25.5	26.0	28.30
98.7	38.7	32.0	37.0	43.30

TABLE 24. Water content of toluene and xylene in equilibrium with H_2SO_4 - water mixtures at 40° C.

Relative humidity (%)	Mg. water in 50 cc of liquid	
	Toluene	Xylene
10	5.76	6.82
30	12.16	10.85
50	18.24	16.42
70	24.00	20.61
90	29.76	26.21
98.7	31.10	26.98

TABLE 25. Moisture content of soils and silica in equilibrium with various humidities.

Humidity (%)	Moisture content (%)			
	Silica	Soil P.C. 66	P.C. 109	P.C. 145
10	4.43	0.92	0.32	2.87
30	6.28	1.10	0.68	4.68
50	7.89	1.17	0.71	7.50
70	12.54	1.25	1.31	9.23
90	24.98	1.88	1.78	12.17
98.7	61.96	2.48	2.30	14.60

each case is fairly close, considering the errors involved in the measurements. The results with capillary systems at low humidities are especially important in view of the fact that it is at low humidities that a difference of opinion exists as to the nature of adsorption. Fortunately, the method is actually more sensitive at

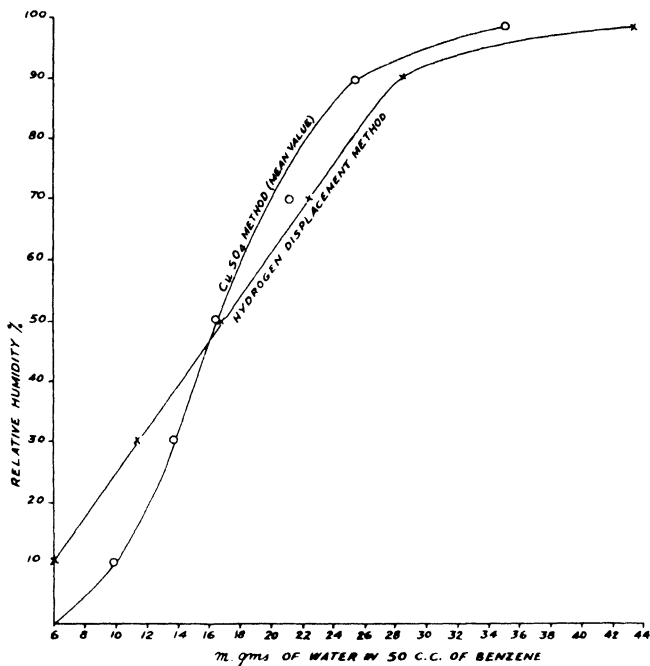



Fig. 29. Relation Between Vapor Pressure of H_2SO_4 - Water Mixtures and Water Content of Benzene in Equilibrium with it at 40°C

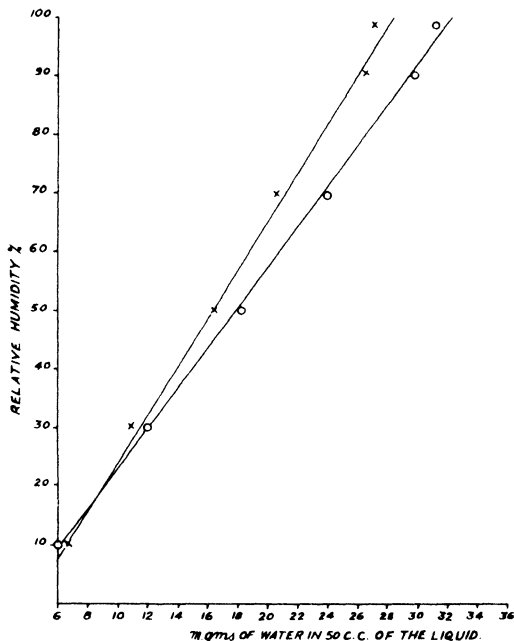



Fig. 30. Relation Between Vapor Pressure of H_2SO_4 - Water Mixtures and Water Content of Toluene and Xylene in Equilibrium with it at 40°C

low humidities and leaves no doubt as to the nature of the forces involved, which must be considered to be the same as those involved at higher humidities, namely, capillary condensation. It is true that those who consider the forces of adsorption to be of an electrical nature might like to bring in a change in the dielectric constant of the medium in which the forces operate. But any such explanation will not be capable of mathematical analysis, as is possible if the moisture absorption is regarded as condensation in minute capillaries subject to the laws of surface tension so well known in the case of macro-capillaries.

TABLE 26. Calculated and found values of moisture in organic liquids in equilibrium with moist soils and silica kept at different humidities.

Relative Humidity (%)	Weight of water in milligrams in 50 cc of moist organic liquid								
	Benzene (H displacement method)			Toluene (H displacement method)			Xylene (H displacement method)		
	Soil No. 145	Silica		Soil No. 109	Silica		Soil No. 66	Silica	
	(found)	(found)	(calc)	(found)	(found)	(calc)	(found)	(found)	(calc)
10	11.0	10.8	11.75	10.976	10.91	13.1	10.30	10.32	11.5
30	14.8	15.2	17.2	16.35	16.42	20.0	14.94	14.98	17.6
50	19.69	23.3	22.75	22.02	21.98	24.3	19.36	19.46	21.0
70	24.92	25.5	25.96	27.29	27.17	28.0	23.84	23.94	24.5
90	32.27	29.3	31.2	30.27	30.30	30.65	26.91	26.53	26.9
98.7	44.98	41.8	44.46	31.33	31.42	31.52	27.17	27.07	27.12

TABLE 27. Corresponding values of relative humidities of water-air and water-ether interfaces.

Relative humidity water-air interface (%)	Relative humidity water-ether interface (%)
5	65.16
10	71.94
30	84.14
50	90.78
70	95.0
90	98.5
99	99.7

There is yet another line of attack on the same problem. We can study the effect of changes in surface tension by placing soils in the joint atmospheres of water and organic liquids such as ether or alcohol, one immiscible and the other miscible with water. Ether, being more volatile, would condense first in the capillary spaces. Since at corresponding humidities the same capillary spaces are involved, water will have to dislodge ether, instead of air, from the interstitial spaces; and thus the surface forces involved would be given by the interfacial tension between water and ether instead of the surface tension between water and air, which is the case when soils are placed in atmospheres of water vapor alone. Making allowances for the change in surface tension resulting from the introduction of an additional liquid phase in the capillary spaces, it

should be possible to calculate the change in vapor pressure at the interface by employing the procedure described before.

The values of relative humidities for the ether-water interface corresponding to different values for the air-water interface are given in Table 27, which can be plotted and intermediate values interpolated. The implication of the values given in Table 27 is that the amount of water absorbed, for instance, from 71.94% humidity of water vapors in the absence of ether vapors would be the same as that taken up from 10% humidity in the presence of ether vapors. Therefore, the amount of ether held up in capillary spaces corresponding to a 10 to 71.94% humidity interval (of water) cannot be dislodged by water. Thus soil in equilibrium with combined vapor pressure of ether and water vapor, both corresponding to 71.94% relative humidity of water, would contain ether and water held up in the following manner:

Capillary spaces corresponding to 0-10% relative humidity of water.	Capillary spaces corresponding to 10-71.94% relative humidity of water.
Filled with water.	Filled with ether.

The amount of water absorbed is interpolated from the moisture absorption-vapor pressure curve of the soil corresponding to the required humidity (10% in this case) and the amount of ether held up can be calculated, since the volume of ether held up in the capillary spaces mentioned above must be equal to that of the water absorbed between 10 and 71.94% humidity. Knowing the latter from the moisture absorption-vapor pressure relationship, the weight of ether is determined from the knowledge of its density. In this manner the percentage by weight of "total liquid" absorbed from different joint humidities of water and ether can be calculated.

The method of calculation may be illustrated by taking the case of P.C. 13 soil when placed in the joint atmosphere of 30% humidity of water and of corresponding humidity of ether.

(a) 30% humidity of water in the presence of ether corresponds to 2.5% humidity of water alone (interpolation from data in Table 27).

(b) Moisture absorbed from 2.5% humidity of water equals 0.62% (interpolated from the vapor pressure curve of the soil).

(c) Moisture absorbed between 2.5 and 30% humidity of water equals 3.23% (interpolated from the vapor pressure curve of the soil).

(d) Volume of ether absorbed per 100 grams of soil is equal to 3.23 cc or the weight of ether absorbed is equal to 3.23 x 0.72, equal to 2.326 grams.

Therefore, the total weight of water and ether absorbed per 100 grams of soil equals 0.62 plus 2.326, or 2.946 grams. The deter-

mined value is 3.14 grams.

Similarly, the values for other soils and other humidities can be calculated.

Eight soils were selected and the determinations of vapor absorption were made at 30%, 50% and 70% of water in the presence of ether vapors of corresponding humidity (*i.e.*, 68%, 79% and 90%). The determined and the calculated values are given in Table 28. The agreement is seen to be fairly close, considering the errors involved in an experiment of this nature. The values of moisture

TABLE 28. Absorption of vapors by soils from the joint atmospheres of water and ether vapors of corresponding humidities.

Soil No. P.C.	30% humidity			50% humidity			70% humidity		
	D	C	A	D	C	A	D	C	A
6	0.53	0.62	0.82	-	-	-	-	-	-
13	3.14	2.95	3.85	6.05	5.93	7.75	8.7	7.11	9.0
123	1.80	1.71	2.14	3.42	3.43	4.5	4.45	3.97	5.03
154	0.48	0.74	0.96	0.9	1.14	1.45	1.35	1.31	1.67
167	0.26	0.29	0.38	0.70	0.82	1.10	1.10	0.89	1.15
212	0.40	0.51	0.67	1.0	1.12	1.50	1.37	1.56	2.05
227	0.40	0.43	0.56	0.85	0.70	0.90	1.25	1.01	1.28
296	0.27	0.32	0.41	0.50	0.66	0.85	0.95	0.79	0.96

D = determined
C = calculated
A = In the absence of ether vapors

TABLE 29. Corresponding humidities of water in the presence and absence of alcohol vapors.

Relative humidity with water vapor alone (%)	Corresponding humidity in presence of alcohol vapors (%)
10	38.37
30	60.53
50	74.97
70	86.22
90	95.72

absorption from the same humidities in the absence of ether vapors were also included in the table for the purpose of comparison.

Further experiments along similar lines were made with combined vapors of alcohol and water. Since these two liquids are miscible, the only change in surface tension involved is due to mixing of two liquids, the new value of surface tension being equal to that of water-alcohol mixtures. If alcohol and water vapors are at corresponding humidities, we may assume that nearly equal amounts of these liquids will condense in the capillary spaces. The surface tension of a mixture of equal amounts of alcohol and water is 28.9 dynes, and its density is 0.926. The values for humidities under changed conditions corresponding to those when water vapors alone

are present are given in Table 29. These values can be plotted and give a smooth curve from which intermediate values can be interpolated. They indicate that the liquid absorbed from say 60.53% humidity of water vapors in the presence of alcohol vapors would be equal to the moisture absorbed from 50% humidity of water vapors when present alone, and so on.

The determinations were made on 8 soils at 30%, 50%, 70% and

TABLE 30. Absorption of vapors by soils from the joint atmospheres of water and alcohol vapors of corresponding humidities.

Soil No. P.C.	30% humidity			50% humidity			70% humidity			90% humidity		
	D	C	A	D	C	A	D	C	A	D	C	A
6	0.45	0.26	0.82	0.4	0.6	1.2	0.9	1.04	1.27	1.3	1.97	3.35
13	3.0	1.5	3.85	6.2	3.15	7.75	5.1	5.98	9.0	7.7	9.9	11.8
123	1.65	0.85	2.14	3.2	1.75	4.5	3.35	3.52	5.03	5.9	6.6	9.95
154	0.6	0.4	0.96	0.6	0.80	1.45	0.75	1.20	1.67	1.15	2.0	2.98
167	0.23	0.15	0.38	0.1	0.31	1.1	0.35	0.70	1.15	0.6	1.4	2.0
212	0.35	0.20	0.67	0.4	0.5	1.05	0.55	1.08	2.05	0.8	2.2	2.60
227	0.12	0.21	0.56	0.2	0.45	0.9	0.45	0.75	1.28	0.9	1.5	2.35
296	0.20	0.24	0.41	0.2	0.40	0.85	0.40	0.60	0.96	0.6	1.2	1.95

D = Determined
C = Calculated
A = In the absence of alcohol vapors

90% relative humidity of water in the presence of alcohol vapors of corresponding humidities, 62%, 77%, 82% and 96%, respectively. The results are given in Table 30 together with the calculated values, which are nothing but the amounts of moisture absorbed from 6%, 19%, 42.5% and 77.5% humidity of water vapor alone, which are interpolated from the moisture absorption-vapor pressure curves of the various soils. The results show fair agreement between the determined and calculated values in the majority of cases. The values of moisture absorption from a particular humidity in the absence of alcohol vapors are also included in the table for the sake of comparison.

It must be admitted that in these calculations so many interpolations are involved that one cannot expect any better agreement. Even if the results are accepted as quasi-quantitative, one cannot help being struck with their general trend, which supports the capillary condensation theory of soil moisture.

CHAPTER VII

BOILING POINT OF WATER HELD IN SOILS AT DIFFERENT VAPOR PRESSURES

The thermodynamic relationship between lowering of the freezing point and rise of the boiling point is well known. The lowering of the vapor pressure consequent upon the absorption of water by soils at once leads to the logical conclusion that a corresponding rise in the boiling point of the water held in the micropores of the soils could be expected. The difficulty of measuring the boiling point of the water held by solid can well be imagined and an apparatus had to be designed especially for the purpose.

Description of the Apparatus

The new apparatus (Fig. 31) for measuring the boiling points and vapor pressure of liquids consists of a brass box capable of being tightly closed with a screwed-on lid consisting of a brass diaphragm mounted on a massive flange. The brass diaphragm is made from a brass sheet 0.22 mm thick by pressing it in a die that produces corrugations. It is interchangeable and can be replaced by a fresh one by unscrewing the flange. After ten to fifteen measurements its elasticity shows signs of fatigue; it is then rejected and replaced by a new one. The cylinderical brass box has a side tube with a stop-cock for evacuating it. On the brass diaphragm is mounted a vertical needle the top of which is focussed against a travelling microscope to record the movement of the diaphragm due to changes in the pressure inside the box. The whole apparatus is immersed in a paraffin bath which can be gradually heated with efficient stirring. The diaphragm needle has two fixed points, one with the top open to the atmosphere and the other when the box is evacuated. The intermediate readings, corresponding to different vapor pressures, are determined by liquids of known vapor pressures.

The boiling point of a liquid is the temperature at which its vapor pressure becomes equal to the atmospheric pressure. The technique for determining vapor pressure, therefore, is very simple. After placing the substance in the box the zero reading is taken with the tap open. The apparatus is then evacuated and the soil bath gradually heated until the needle again records the zero reading. The temperature corresponding to that is recorded as the boiling point.

The arrangement for taking readings with a travelling microscope is preferable on an instrument of this nature. A better method would appear to be to incorporate some lever arrangement that would work a needle against a graduated dial. Any desired magnification of the movement of the diaphragm can thus be obtained. An arrangement of this nature, however, may be subject to errors due to friction, since the entire apparatus has to be heated in an oil bath.

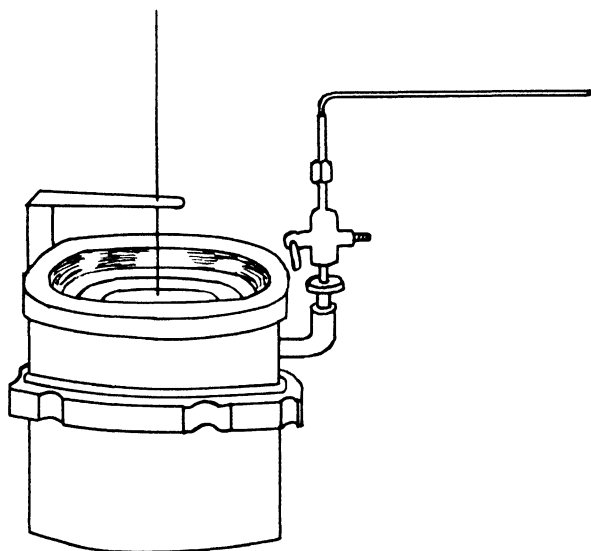



Fig. 31. Apparatus for Determining Boiling Point of Soils

TABLE 31. Boiling points of various liquids.

Liquid	Boiling point	
	Found (°C)	Actual (°C)
Water	100.0	100.0
Ethyl alcohol	78.0	78.35
Secondry Amyl Alcohol	118.5	119.8
Xylene	136.0	137.0
Toluene	113.0	110.6
Benzene	80.0	80.1

Boiling points of a number of liquids were first determined for finding the accuracy of the apparatus (Table 31).

Thermal Expansion of the Apparatus

To calibrate the instrument it appeared necessary first to study the effect of temperature on the rise and fall of the diaphragm. The changes in the height of the needle were noted during the gradual rise of temperature with the top open (atmospheric pressure) and

when the apparatus was evacuated. Obviously the ideal condition would be if there was no change in the level of the needle with a rise or fall of temperature. The following observations (Table 32) show that the change is slight. The readings were confirmed by several repetitions.

It appeared that erratic results were obtained without efficient stirring. It is, therefore, very important that the apparatus should be allowed to attain the temperature of the bath, and this can only be done by efficient stirring of the paraffin bath and very gradual heating (a rise of temperature of not more than 1°C per minute).

The manner of heating the paraffin bath is important. A good deal of time was wasted in the first instance when the bath was heated with gas burners. It was noticed that as soon as the burner was lighted there was a sudden change in the level of the indicator needle because the vapor pressure apparatus which was touching the bottom of the copper bath took up heat before the paraffin in the

TABLE 32. Readings of the empty boiling point apparatus with rise and fall of temperature.

Temperature (°C)	Heating	Cooling
28	22.92	22.89
30	22.92	22.89
40	22.92	22.89
50	22.92	22.90
60	22.92	22.90
70	22.96	22.92
80	23.01	22.99
90	23.06	

bath had time to equalize the temperature. The results appeared very puzzling at first, until by a process of elimination the trouble was traced to the source of heat. Subsequently this source of error was completely eliminated by the use of an electric immersion heater.

The perfection of this apparently simple apparatus entailed a good deal of long and laborious work. In the preliminary stages several sets of observations had to be rejected when a source of error was discovered at a later date. For instance, the liquid or the soil of which the boiling point is to be measured must be in close contact with the metallic base of the vapor-pressure apparatus. The failure to recognize this fact led to the rejection of a whole series of observations with sulphuric acid-water mixtures when it was later discovered that the porcelain dish in which the mixture was held caused so much lag in the transmission of heat that the boiling points were obtained several degrees higher than the theoretical values. Curiously enough, the soil was also influenced by the same factor, namely the lag in heat transmission. The trouble in both cases was removed, in the first case by lead dishes for containing

sulphuric acid-water mixtures, which were in immediate contact with the walls of the vapor-pressure apparatus, and in the second case by using not more than ten grams of the sample spread evenly on the bottom of the apparatus. It is very essential that the thickness of the soil layer should not exceed a few millimeters.

The thermodynamic relationship between the rise of boiling point (T) and relative vapor pressure $(\frac{p'}{p})$ may be briefly summarized as follows:

$$T = \frac{(1-p'/p)}{0.03438}$$

If this relation could be proved to hold good with soils of known vapor pressures, it would constitute a strong evidence in favor of the view that moisture in the soils and other capillary systems is held in the micropores subject to the forces involved in surface-tension effects. All moisture right up to the point that this relation is found to be true must be reckoned as "capillary condensed" and not "adsorbed" in any other sense.

Calibration of the Instrument

To see if the movement of the diaphragm and hence of the indicator needle is strictly proportional to the change in vapor pressure, observations were taken with pure distilled water which was gradually heated to the boiling point after evacuating the apparatus. The position of the needle at various temperatures as observed in the travelling microscope was recorded. These readings, when plotted against the known values of vapor pressures at corresponding temperatures, give a straight-line curve showing perfect correlation (Figure 32). Boiling points of a number of pure liquids and solutions were then determined with this apparatus. The results given in Table 33 show that it could be depended upon to give reasonably accurate values for boiling points.

Variation of Vapor Pressure with Temperature

The boiling-point apparatus appears to be ideal for studying changes in the vapor pressure with temperature, since there is a linear relationship between the movement of the diaphragm and change in pressure.

The ease with which the vapor pressure of a liquid at the boiling point (1 atmosphere) can be determined renders this apparatus extremely useful for finding the vapor pressure of liquids at different temperatures. There are two methods of approach to this problem. If the vapor pressure of a liquid at ordinary temperature is known, then the movement of the indicator needle will give at once the proportionate change in its vapor pressure due to temperature. On the other hand, if we determine the boiling point of a liquid, then assuming that at this temperature its vapor pressure is equal to

atmospheric pressure in mm of mercury, we can work backward and obtain the vapor pressures at different temperatures from the readings of the needle level. This instrument, therefore, can be used for finding the vapor pressure of any liquid at any temperature.

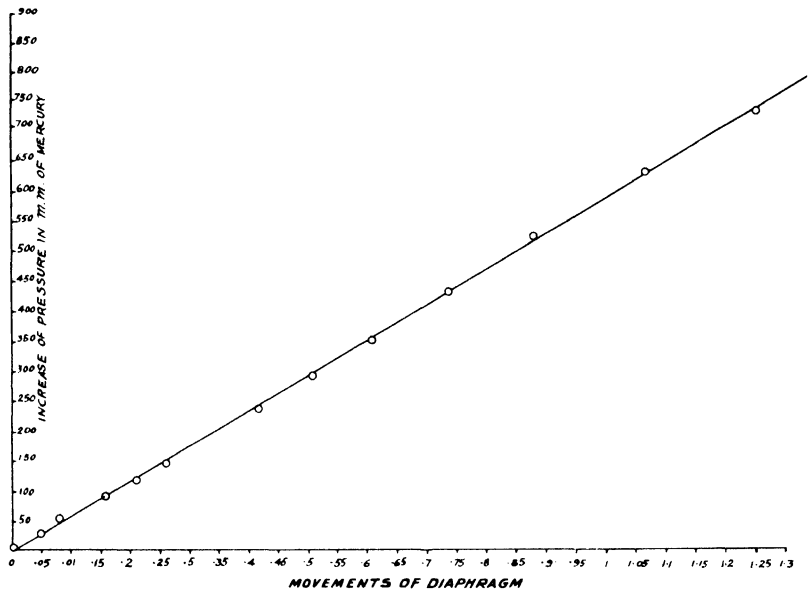



Fig. 32. Relation Between Movements of Diaphragm and Change of Pressure in Terms of mm of Mercury

TABLE 33. Boiling points of various solutions.

Solution	Molar concentration	Relative humidity %	Observed B.P. (°C)	Calculated B.P. (°C)
Sugar	4	90	103	102.88
	6.5	83	105	104.9
$ZnCl_2$	17	12.6	128	125.3
	11	34.8	120	119.3
$CaCl_2$	7	33.5	117	119.3
	5	51.5	110	114.4
	3	75.0	105.6	108.64
H_2SO_4	0.5	99	100.5	100.28
	2	90.9	102	102.88
	4	70.0	109.5	108.64
	5.5	50.0	116.5	114.4
	7	30.0	121	120.2
	9.5	10.0	126	125.9

The vapor pressures of methyl alcohol, ethyl alcohol and xylene were determined in this manner, both from their known vapor pressure at a particular temperature and from the boiling point. The results are plotted in Figure 33, along with the known values from

"International Critical Tables." The determined values are remarkably close to the known values, thus proving the utility of this apparatus. Since the determination of vapor pressures by both static and dynamic methods is extremely tedious, the value of this simple apparatus will at once be recognized.

Having established the reliability of the apparatus with pure liquids and solutions, a number of soils of diverse character were examined. Some fundamental characteristics of these soils are recorded in Tables 34 and 35, to bring out the wide divergence in their properties.

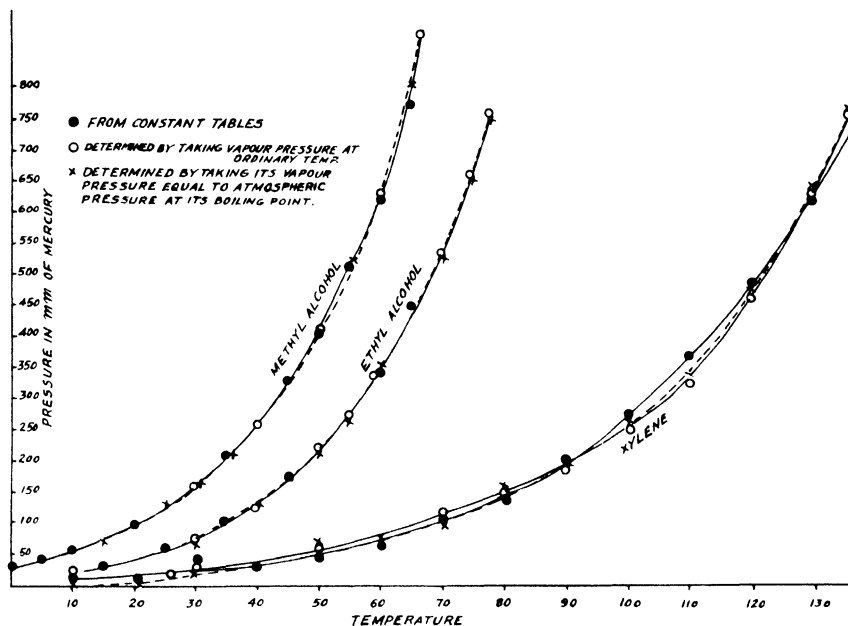



Fig. 33. Vapor Pressure of Various Liquids at Different Temperatures

The soils were brought into equilibrium with sulphuric acid-water mixtures of different vapor pressures by prolonged exposure in desiccators. Ten grams of the soil of known humidity were then spread in a thin layer in the brass cup of the vapor-pressure apparatus, which was then evacuated and gradually heated. The temperature at which the indicator needle registered the atmospheric pressure was taken as the boiling point of the water in the moist soil in every case.

During the process of heating there is some loss of moisture by the soil. This is no more than the amount of vapor required to fill the brass cup, and cannot make any appreciable difference in the moisture content of the soil. One great merit of this apparatus is that the moisture content of the soil or the composition of the solution under examination does not undergo any appreciable change during the determination of the boiling point. The relative vapor

pressures and boiling points of soils, both determined and calculated, are given in Table 36.

Irrespective of the nature of the soil or its moisture content at a particular humidity, the boiling point is a function of the vapor

TABLE 34. Single-value constants of soils used in vapor-pressure studies.

Soil No. P.C.	Clay % .002 mm	Ultra Clay % .0001 mm	Exchangeable bases (m.e./100 g of soil)		
			Ca	Na plus K	pH
6	28.4	16.9	6.3	1.0	5.29
13	60.3	41.0	55.6	3.3	8.53
72	45.9	11.4	14.0	1.8	8.30
123	85.5	30.2	12.0	17.4	8.92
141	54.5		50.4	1.0	9.03
145	62.2	60.1	54.2	3.6	8.30
161	41.1	28.6	34.2	1.0	7.68

TABLE 35. Moisture absorption of soils at different humidities.

Soil No. P.C.	Moisture at					
	10%	30%	50%	70%	90%	99%
6	1.06	1.42	1.79	2.76	4.32	7.51
13	4.10	7.34	8.59	11.07	12.89	16.79
72	0.06	1.2	2.01	2.43	4.07	6.43
123	0.74	3.31	4.35	7.25	10.63	14.32
141	1.59	3.11	6.40	9.87	11.32	13.66
145	2.88	4.58	7.46	9.19	12.05	14.58
161	1.14	2.28	3.18	4.54	6.16	9.55
Silica	8.99	16.25	24.97	30.06	39.05	51.0

TABLE 36. Boiling point of soils at different vapor pressures.

Soil No. P.C.	Boiling points at various humidities (°C)					
	10%	30%	50%	70%	90%	99%
6	127.0	120.0	114.0	106.5	104.0	100.0
13	126.5	123.0	116.0	108.0	104.0	100.0
72	128.5	121.5	118.5	107.5	104.0	100.0
123	125.5	119.5	116.0	107.0	103.5	100.0
141	126.0	120.0	114.0	106.5	101.0	100.0
145	125.0	119.0	113.5	106.5	102.5	100.5
161	127.0	124.0	115.0	106.0	104.0	100.0
Silica	124.0	119.0	114.0	107.0	101.0	99.5
Calculated B.P.	125.92	120.2	114.4	108.6	102.9	100.3

pressure and the calculated values of boiling points from thermodynamic relationship are almost exactly equal to the experimentally determined values for all soils at all humidities down to the lowest value, at which the size of the micropores is of the order of only a few molecules. These results are of far-reaching consequence and would leave no doubt that beyond perhaps a monomolecular layer all moisture in the soil must be considered as capillary condensed.

CHAPTER VIII

HYSTERESIS EFFECT IN CAPILLARY MOISTURE

As stated before, there exist two distinct series of equilibrium values between moisture content and pressure deficiency or relative humidity, both for capillary and for hygroscopic moisture, which correspond to the two directions in which the moisture changes can be carried out. The moisture content in both cases is always higher when the state of equilibrium has been reached from the wetter state than when reached from the drier state. The "drying" and "wetting" curves form two distinct series, which can be reproduced any number of times by alternate drying and rewetting. This similarity in the behavior of capillary and hygroscopic moisture is the first indication that the two are essentially alike, and that in the case of hygroscopic moisture we are perhaps dealing with capillary condensation. The hysteresis effect is a necessary concomitant of variations in capillary moisture. Experimental proof for the existence of the two series of equilibrium values constituting the hysteresis loop has already been given. The theoretical justification has been developed by Haines and is given below in his own words:

"Let us consider the simplest case of a cellular capillary tube, that is, one which has regular constrictions of diameter at intervals along its length. Such a tube is depicted in Figure 34. The film shape of an air-water interface in this tube will always approximate a hemispherical meniscus, giving rise to a suction or pressure deficiency on the water side of the film of a magnitude depending on the diameter of the tube according to the well known formula $p = 2T/r$, where T is the surface tension and r is the radius of the tube at the point where the meniscus stands. Suppose such a tube is to be set in water and slowly raised. The length of the water column will gradually increase, the meniscus maintaining equilibrium by moving slightly into the narrowing section of the tube, which movement increases the curvature of the meniscus till it reaches the narrowest part of the waist in the tube, when we have the maximum height of column (h_1) which can be sustained. The position is now unstable. A slight further movement of the tube causes the meniscus to move to a place of increasing diameter and decreasing suction, so that it slips down to the next narrow place or waist, evacuating in this movement the water from one

(cell). For a continued rise of the tube the meniscus will make these jumps periodically, its height meanwhile rising slowly and falling abruptly between two values which differ slightly, the difference depending on the length of the unit cell.

"Suppose now that the direction of movement of the tube be reversed. The meniscus falls with the movement of the tube, accommodating itself to the reduced pull of the water column by a slight movement into the wider part of the tube. When it reached the

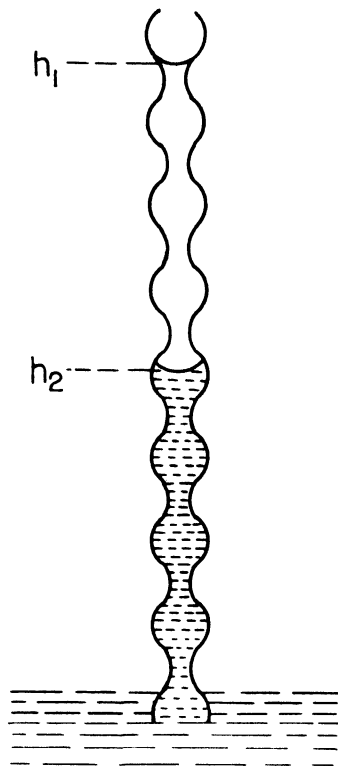



Fig. 34. Rise and Fall of Water in a Cellular Capillary Tube (Haines)

widest part it is again unstable, since it is now in a region of decreasing diameter or increasing suction. The meniscus, therefore, gives a jump upward through the waist to a corresponding position in the next cell. Then ensues a series of changes exactly like the previous series, except that the height of the column in the tube oscillates slightly about a height, h_2, which is considerably lower than in the other case. The tube, therefore, shows two main suction values according to whether it is being filled with, or emptied of water, the two values corresponding to the maximum and minimum diameters of the tube. Although the pore-space of the soil has a more intricate character than this simple tube, yet it shows the same essentials in its behaviour."

McBain, without referring to Haines' work, apparently quite independently, put forward a somewhat similar explanation. The essential feature of the pores in both cases is that larger cavities are accessible only through smaller channels or orifices. Rao in a series of papers has accepted the explanation of cavities with constricted ends, and has proved the permanence and reproducibility of the hysteresis loop in the sorption of water and carbon tetrachloride on titania, silica and ferric oxide gel. During a series of sorptions and desorptions of ferric oxide gel a certain amount of drift was noticed in the hysteresis loop; this is ascribed to a progressive widening of the cavities, and their necks. It is also assumed that the tail end of the hysteresis loop can extend up to zero pressure only if there are in the porous adsorbent cavities having necks of molecular diameter. This tacitly assumes that capillary condensation extends down to capillaries of molecular dimensions - an assumption that is not accepted by McBain, who is inclined to associate the entire phenomenon of capillary condensation with moderately high relative humidities.

To explain the phenomenon of "drift" with other changes of the hysteresis loop in the sorption of water on ferric oxide gel, Rao and Theruvenkatachar advanced the theory of the coalescence of the particles of the porous system accompanying successive sorption and desorption. In support of this theory a mathematical formulation has been made which relates the cavity volume with particle radius. The formula indicates that, mass remaining the same, the total cavity volume decreases as particle radius increases. Since it is the cavity volume that is supposed to determine the magnitude of the hysteresis effect, the latter would be greater in fine-textured soils than in coarse sands. This conclusion is capable of verification and, as will be shown later, there appears to be no relation between the mean diameter of soils and silts and the magnitude of the hysteresis effect.

The essential feature of the argument advanced by Haines and others is the cellular structure of the pores, given by an assemblage of grains which have mainly convex surfaces. They argue that in whatever irregular a fashion the cross-section of the pores may vary, the whole system must be like a network composed of wider cell-like spaces communicating through narrower channels which, when stretched out in a single row, exhibit in a simplified form the capillary properties of such a pore space. Similar reasoning, therefore, would not apply to an assemblage of capillary pores not communicating with one another and each having an independent existence. Nor would it apply to a single capillary tube or a bundle of tubes.

This is a serious drawback in the whole line of argument, even granting that all capillary systems would probably conform to this pattern. For this purpose we shall take the simplest case of a capillary tube full of liquid, the lower end of which is connected

through a rubber tube to a burette exactly as in the capillarimeter described before (Figure 35). With this apparatus we can follow the changes in the level of the liquid in the capillary tube when the burette tube is gradually lowered and raised.

The results of an actual experiment with a capillary tube of 0.154 mm diameter bore are plotted in Figure 36. The application of pressure deficiency results in no movement of water in the capillary tube until the burette tube has been lowered by a distance $h = 2T/r$, where T is the surface tension of the liquid and r the radius of the capillary tube. Henceforth any lowering of burette

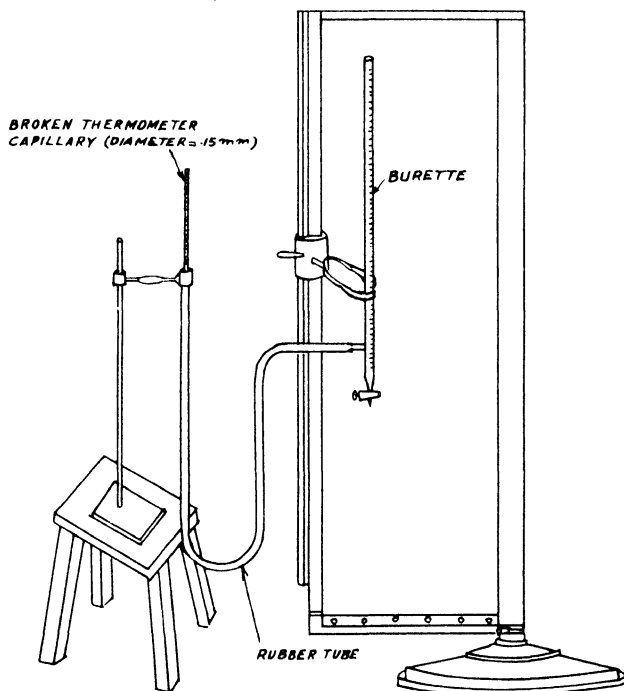



Fig. 35. Apparatus for Finding Hysteresis Effect in the Rise and Fall of a Liquid in a Capillary Tube

tube should theoretically result in a corresponding decrease in the level of the liquid in the capillary tube. When the zero mark in the capillary tube has been reached, the burette tube is gradually raised stepwise. In the absence of any hysteresis effect the rise of liquid level should retrace on the same line; instead of doing so, it shows a well defined hysteresis effect, which can be reproduced backward and forward as many times as one likes. In an actual experiment using kerosine this was done four times and as will be seen from Figure 37, the hysteresis loop is reproducible.

The following liquids were next tried: kerosine, glycol, glycerin, aniline and liquid paraffin. The capillary tube used was 30 cm long and had a bore of 0.154 mm diameter. It was connected to a burette

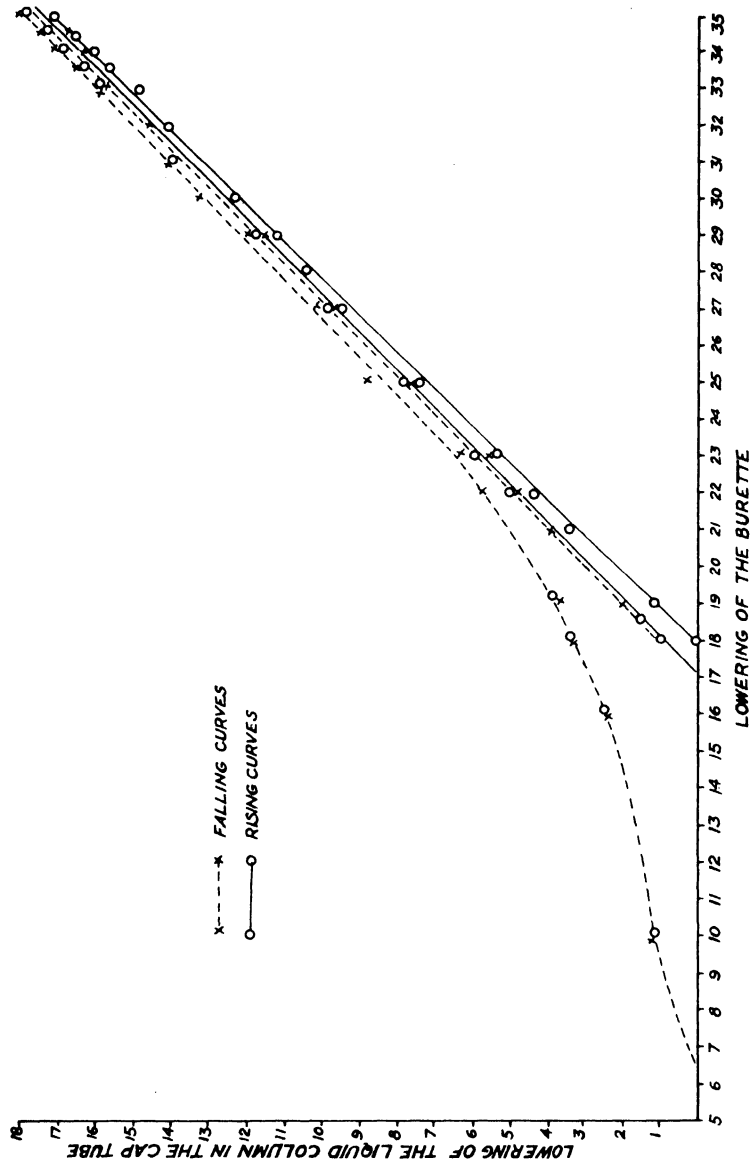



Fig. 36. Change in Liquid Level in a Capillary Tube

tube through a pressure tube in the capillarimeter. The results obtained in the case of various liquids are plotted in Figures 38, 39, 40 and 41. The magnitude of the hysteresis effect for purposes of comparison may be obtained by taking the ratio of the areas to the left of each of the falling and rising areas. The higher the ratio the greater the hysteresis effect. When the ratio is 1 there is no hysteresis effect. These ratios in the case of various liquids are given in Table 37.

It appears that there is no correlation between the magnitude of the hysteresis effect and physical properties of a liquid, such as surface tension and viscosity, though there is a slight indication of

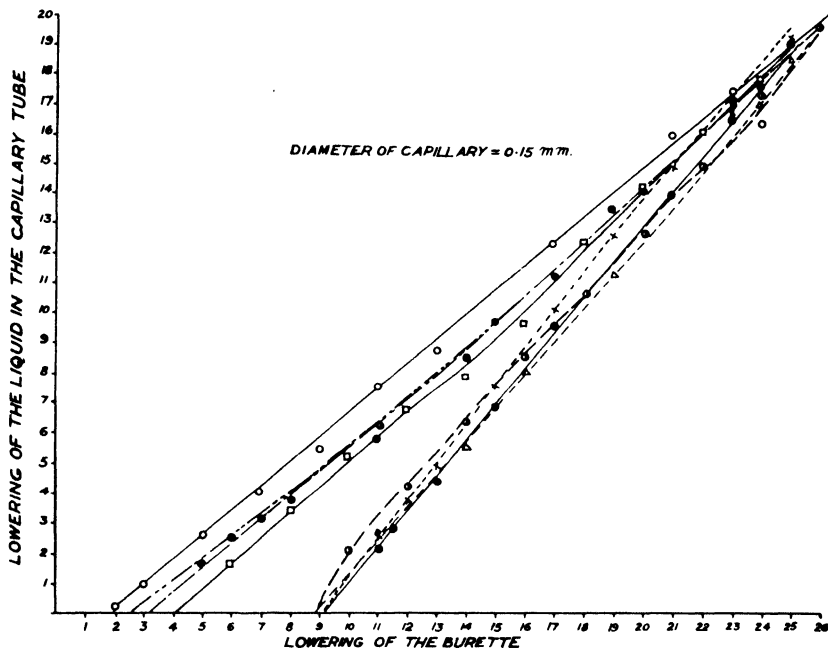



Fig. 37. Reproducibility of Hysteresis Effect with Kerosene Oil in a Capillary Tube of 0.15mm Diameter

an increase in the ratio with increase in viscosity.

These experiments afford a very simple explanation of the hysteresis effect in capillary systems. It can be due only to the frictional resistance between the walls of the capillary and the rising or falling liquid, and its magnitude must be a function of the contact angle, the wetting power and the viscosity of the liquid, or the shearing stress of the molecules. The variations in the contact angle with the advancing or receding capillary front were observed by Rayleigh as early as 1890. This variation was explained by Adam and Jessop as due to friction of the liquid on the solid. They showed how its effect on the measurement of contact angle can be eliminated by taking two measurements: one when the liquid is on the

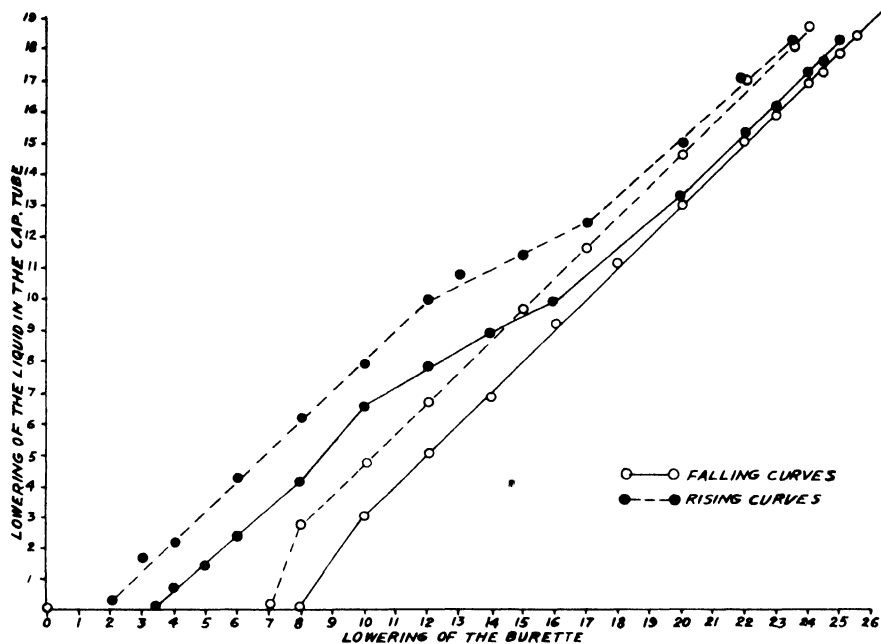



Fig. 38. Hysteresis Effect with Glycol in a Capillary Tube of 0.15mm Diameter

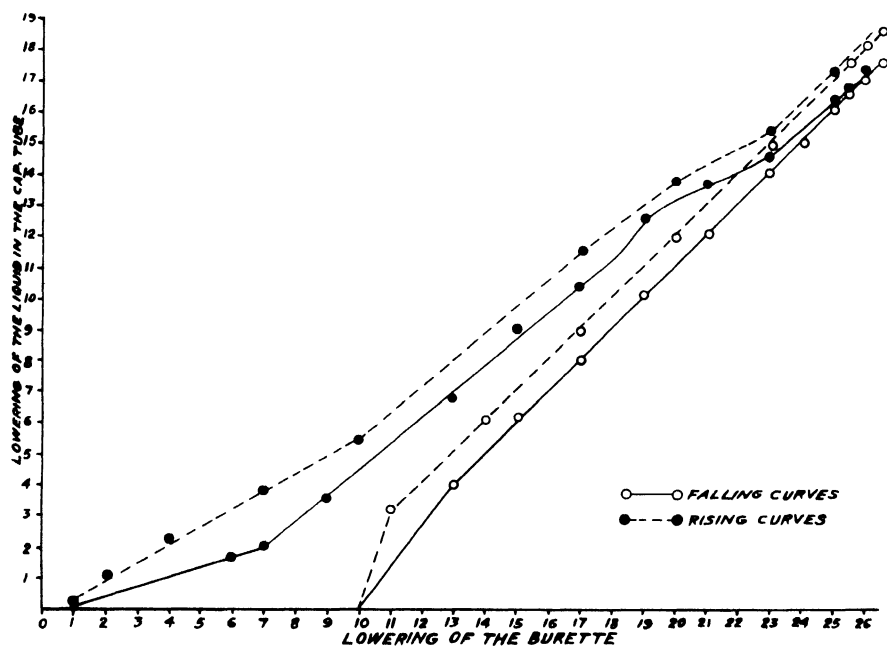



Fig. 39. Hysteresis Effect with Aniline in a Capillary Tube of 0.15mm Diameter

point of advancing and one when it is on the point of receding. The mean of the two values is taken as the measure of the true contact angle. It is assumed that the contact angle is zero only if the liquid is receding. With the advancing capillary front the contact

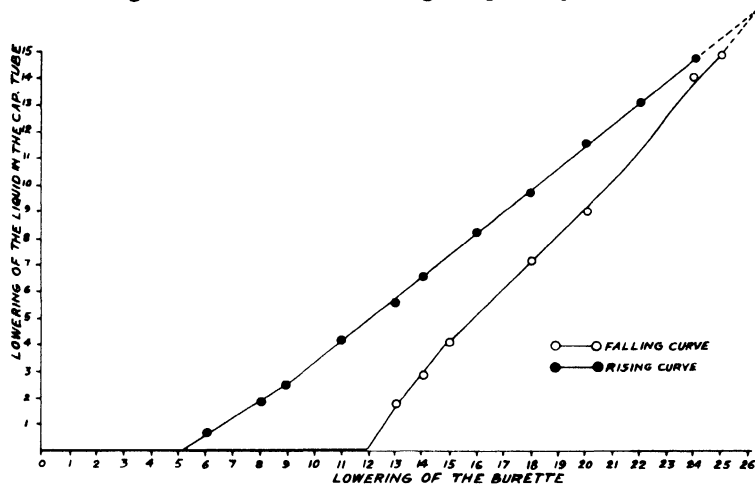



Fig. 40. Hysteresis Effect with Glycerene in a Capillary Tube of 0.15mm Diameter

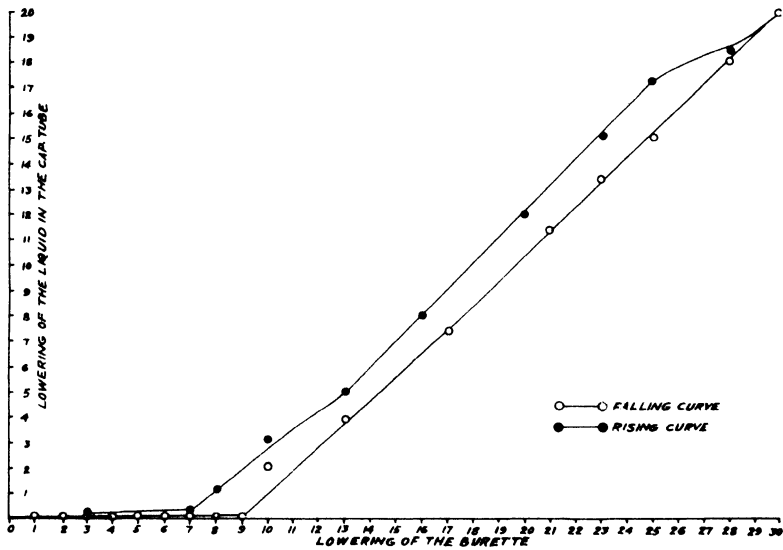



Fig. 41. Hysteresis Effect with Paraffin Liquid in a Capillary Tube of 0.15mm Diameter

angle may assume finite values, and that is why in the measurement of surface tension the capillary height is measured with a falling meniscus.

Experiments with Capillary Tubes Having Blown-in Bulbs

In order to simulate the conditions existing in capillary tubes with structure of the type described by Haines (Fig. 34) experiments were conducted with a capillary tube of 0.57 mm bore, having bulbs blown in between at intervals of about 2.7 cm. The first bulb was 7 cm from the top. The capillary was filled with the liquid up to the top and the liquid in the burette tube was adjusted at the same level. The burette was then gradually lowered and the

TABLE 37. Magnitude of hysterisis effect in a capillary tube with various liquids.

Liquid	Area (a) left of falling curve	Area (b) left of rising curve	Ratio a/b
1. Water	468	421	1.111
2. Kerosine Oil	323	290	1.114
3. Glycol	323	278	1.162
4. Aniline	333	311	1.0707
5. Glycerene	278	225	1.230
6. Paraffin liquid	390	342	1.140

corresponding reading of the liquid in the capillary tube was observed by means of the cathetometer as before. The falling as well as the rising curves in the case of water and kerosine are shown in Figures 42 and 43.

In the "falling curve" the line AB represents the region in which the liquid transference from the capillary portion to a bulb takes place; from B onward the liquid again falls into capillary tube. In the case of "rising curve", the region BA denotes the position and behavior of the liquid in the various bulbs. As soon as it reaches A, the liquid suddenly shoots up into the capillary tube till it again enters the next bulb at B. It will be seen that points B along the rising and falling curves more or less coincide, *i.e.*, the points at which the liquid transference from a capillary to a bulb takes place, whether going up or coming down, are almost identical. Hysteresis effect, therefore, is limited to the positions when the liquid falls from capillary into bulb along the "falling curve". or rises from bulb into capillary along the "rising curve". The presence of cellular structure, therefore, is not necessary to explain the hysteresis effect in capillary tubes.

Since mercury does not wet glass and has a contact angle greater than 90°, the hysteresis effect in this case must be in the opposite direction. This is actually the case, as will be seen from Figure 44, in which a capillary tube of 0.154 mm bore was used.

That the contact angle has a profound influence on the relation between pressure deficiency and percentage saturation on the pores in capillary systems is indicated in Figures 44 and 45, in which the effect of greasing the sand particles on capillary moisture rela-

tionship is shown. It must be remembered that the relation $p = 2T/r$ relating pressure deficiency to surface tension and radius of

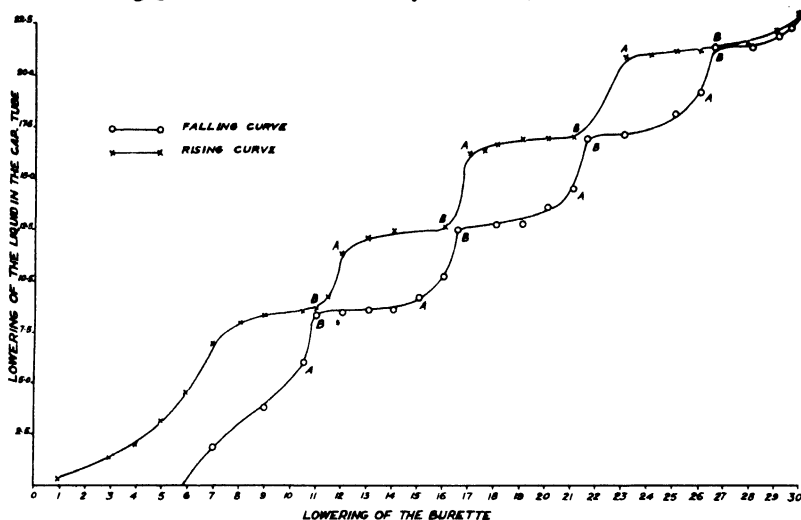



Fig. 42. Hysteresis Effect with Water in a Capillary Tube with Bulbs Blown in Between

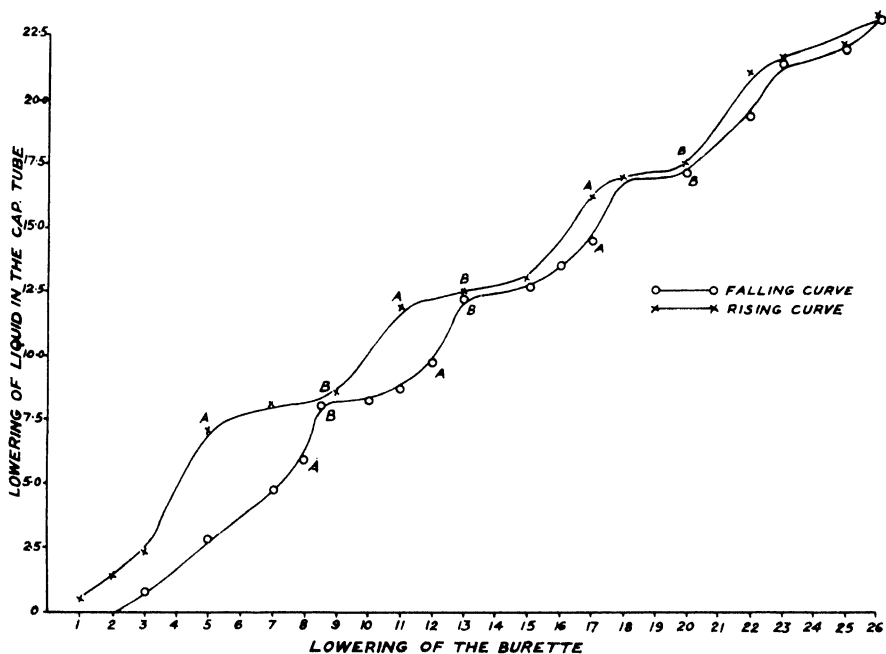



Fig. 43. Hysteresis Effect with Kerosene Oil in a Capillary Tube with Bulbs Blown in Between

the capillary tube is true only in the case of liquids having a contact angle equal to zero. The general relationship $p = 2T/r \cos\theta$ in that case is reduced to $p = 2T/r$, since $\cos\theta$ is equal to unity.

Obviously when Θ has a finite value the moisture distribution must be correspondingly affected.

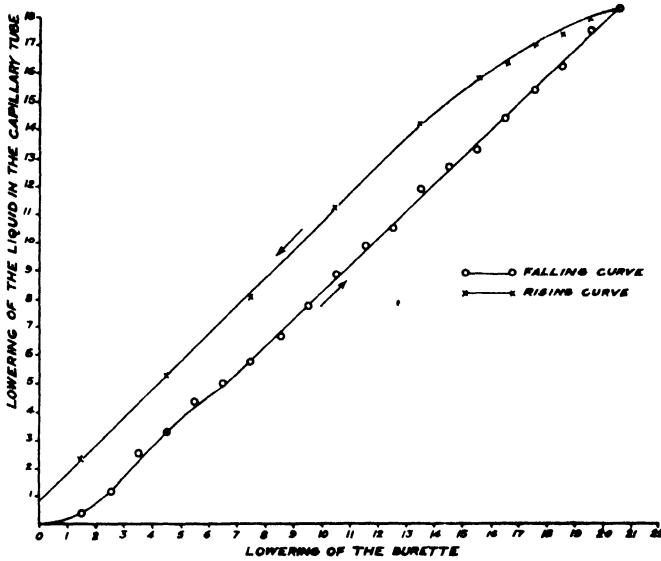



Fig. 44. Hysteresis Effect with Mercury Using Capillary Tube of 0.15mm Diameter

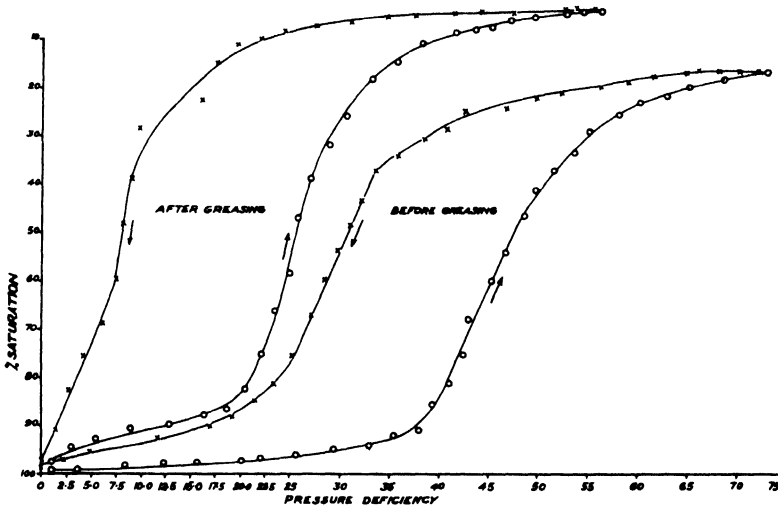



Fig. 45. Pressure Deficiency-Percentage Saturation Curves of Sand Before and After Greasing

As a matter of fact, since this relation has been shown to hold good in the case of soils and silts of varying diameter, provided r is taken as the mean radius of the capillary pores, the "entry value" or the "break point" in the capillarimeter could be used for

measuring the contact angle of a liquid with respect to a powder. This aspect of the question is discussed in Chapter IX.

It will be clear from the discussion in the foregoing that the hysteresis effect is a fundamental property of capillary absorption of liquids; and the fact that both capillary and hygroscopic moisture show this phenomenon is proof that both relate to similar surface-tension effects, and that moisture absorption from the vapor phase at different humidities is due to capillary condensation in micropores down to molecular dimensions. The nature of the moisture absorption curves where micropores are involved is in no way different from pressure deficiency - percentage saturation curves where macropores are involved. The capillary-pressure curves cover only a fraction of the range of the vapor-pressure curves, though both are subject to the same laws of capillarity. It has been shown (Figure 17) that the capillary-pressure curve can be calculated from the size distribution of particles and the laws of capillarity. It has also been shown that the vapor-pressure curve can be calculated from the size distribution of particles, and conversely that the mechanical analysis of particles down to as low as $10^{-6.5}$cm can be calculated when the vapor pressure curve is known.

Whatever explanation of the hysteresis effect is accepted, it cannot be denied that this phenomenon must be associated with capillary condensation; and since it is of a general nature, irrespective of the nature of the liquid or the absorbent, the absorption of vapors of liquids in porous bodies must be ascribed to capillary condensation down to pores of molecular dimensions. Any explanation based on residual valencies or monomolecular layers must be rejected, as such valencies must be specific. Unless we mean something quite different from the valencies associated with chemical reactions, we shall be hard pressed to visualize them in terms of anything tangible.

As the actual mechanism of the hysteresis effect is not vital to the line of agreement adopted in this chapter, no attempt has been made to review the various theories pertaining to this phenomenon, as practically every one is agreed on the point that the hysteresis effect is only associated with capillary condensation. It is interesting to note, however, that Rao, who has made an exhaustive study of the phenomenon and has reviewed all the previous work on the subject agrees that "the explanation based on friction in contact angle, however, though obscure, can account, probably in all cases, for the hysteresis effect and its reproducibility".

It must be admitted that the explanation of cellular structure of the capillaries with narrow necks, though suitable for moisture absorption in the liquid state, would amount to over-stretching the analogy in the case of absorption from the vapor phase; and in view of the clear experimental evidence that a straight capillary tube of uniform bore shows this phenomenon, which is in no way different from that observed in the case of powders or gels, it would be un-

necessary to resort to any explanation other than the very simple one presented in this chapter. If it is argued that the friction in the contact angle is due to the fact that the surface of the capillary tube is not clean, it might be pointed out that no absorbent surface could be expected to be clean and friction in the contact angle could, therefore, be expected in every case.

That contact angle plays a very important role in determining the magnitude of the hysteresis effect is shown by moisture absorption results with stearates, myristates and urates. These compounds

TABLE 38. Moisture contents of stearates, myristates, and urates in equilibrium with different humidities (wetting and drying values).

		Moisture percentage					
		10.4%	30%	50%	71.4%	90.9%	98.7%
Sr Stearate	(i) Drying	0.0	0.0	0.0	0.0	1.23	20.65
	(ii) Wetting	0.0	0.0	0.0	0.0	0.0	3.56
Ca Stearate	(i) Drying	0.0	0.0	0.0	2.05	2.93	5.10
	(ii) Wetting	0.0	0.0	0.0	0.0	0.0	0.98
Ba Stearate	(i) Drying	0.0	3.2	8.23	8.97	9.06	19.28
	(ii) Wetting	0.0	0.0	1.23	3.16	3.05	4.58
Na Stearate	(i) Drying	0.0	0.0	0.0	1.92	2.36	1.97
	(ii) Wetting	0.0	0.0	0.0	0.0	0.0	0.0
Sr Myristate	(i) Drying	0.16	1.23	2.07	9.35	15.61	28.12
	(ii) Wetting	0.0	0.0	0.0	1.905	3.67	7.25
Ca Myristate	(i) Drying	0.0	0.0	0.0	0.0	9.75	21.60
	(ii) Wetting	0.0	0.0	0.0	0.0	2.71	6.52
Ba Myristate	(i) Drying	0.0	0.0	0.95	4.76	5.20	7.16
	(ii) Wetting	0.0	0.0	0.0	0.0	0.0	0.29
Ca Urate	(i) Drying	0.0	0.0	12.35	11.97	17.97	21.21
	(ii) Wetting	0.0	0.0	1.36	2.90	2.56	4.78
Ba Urate	(i) Drying	0.15	0.23	2.96	3.12	11.41	41.46
	(ii) Wetting	0.0	0.0	0.0	0.16	1.82	8.76
Sr Urate	(i) Drying	0.0	0.0	7.60	11.95	17.67	26.40
	(ii) Wetting	0.0	0.0	0.32	3.10	5.6	6.20

are known to have a high contact angle with water. The stearates and myristates were prepared by first precipitating the corresponding fatty acids from alcoholic solution by adding them to water in a thin stream under violent stirring. Fatty acids, when precipitated in this manner, are obtained in a molecularly dispersed state so that they can be neutralized with alkalies like any other soluble acid. The various salts were prepared by neutralizing with equivalent amounts of alkalies. The salts in the wet state were dried at various humidities, and after drying were allowed to absorb mois-

ture at various humidities. The two sets of values corresponding to the drying and wetting curves are given in Table 38. It will be seen that there is enormous difference in the two sets of values.

It is to be remembered that though the magnitude of the hysteresis effect may differ in different substances, the phenomenon is of a general character and common to all substances possessing a

TABLE 39. Hysteresis in moisture absorption-vapor pressure relationships of different substances.

		Moisture absorbed from different humidities					
		10%	30%	50%	71.8%	90.9%	98.7%
1. Coconut charcoal $ZnCl_2$	Drying Wetting	6.34 4.86	9.51 8.87	12.28 11.00	13.10 11.92	15.51 15.59	- -
2. Pistachionut charcoal $ZnCl_2$ treated	Drying Wetting	4.95 3.66	6.22 5.79	8.11 7.44	9.59 9.50	11.70 11.23	- -
3. Pistachionut charcoal heated –10 800 C	Drying Wetting	2.9 0.63	3.5 2.07	8.36 6.19	14.20 9.78	28.10 28.32	- -
4. Filter paper ordinary	Drying Wetting	0.5 0.17	0.59 0.46	2.12 1.7	3.1 2.8	9.36 7.5	- -
5. Hay	Drying Wetting	1.82 0.86	4.1 2.9	6.1 4.9	9.12 7.47	22.01 19.20	- -
6. CO_2 activated coconut husk charcoal	Drying Wetting	3.48 1.66	7.10 4.92	11.4 9.33	18.7 13.55	36.9 42.71	- -
7. Charcoal from $ZnCl_2$ treated coconut shell before carbonization	Drying Wetting	1.40 0.92	7.40 6.36	6.78 6.79	9.09 8.94	10.70 12.16	- -
8. Decolorizing charcoal (a commercial product)	Drying Wetting	4.3 0.87	9.8 5.80	26.6 17.50	48.5 44.30	81.80 81.66	- -

capillary or cellular structure. The results of moisture absorption at various humidities for a few more substances are given in Table 39. A definite hysteresis effect is brought out, as expected.

The existence of the phenomenon of hysteresis in vapor pressure - moisture absorption relationships of all substances with cellular structure is a strong argument in favor of the capillary condensation theory.

CHAPTER IX

MOISTURE ABSORPTION AS INFLUENCED BY CONTACT ANGLE

Liquids rest on solids at a definite angle, known as the contact angle. Its magnitude determines the relative strengths of the adhesion of the liquid to the solid, and to itself. If the contact angle is zero the liquid attracts the solid as much as or more than it attracts itself. A contact angle of 90° indicates that the attraction of liquid for solid is half that for itself, and an angle of 180° would indicate no adhesion between liquid and solid. An angle of 180° is not possible in practice, as there is always some adhesion between a solid and a liquid.

Contact angles have received very little exact study for the very simple reason that they are rarely, if ever, quite definite, the values generally lying between two extremes. These variations are due to the frictional resistance of the liquid against the solid and have already been referred to in the discussion of hysteresis (Chapter VIII).

The simplest method for determining the contact angle is to measure the height of rise of the liquid in a capillary tube of the solid, and then apply the following well known relation:

$$h = \frac{2\gamma \cos\theta}{g r D} \qquad \text{(A)}$$

where h = height of rise of liquid
g = acceleration due to gravity
r = radius of the tube
D = density of the liquid
γ = surface tension of the liquid
θ = contact angle

The application of this equation in the case of soils, silts and sands has been shown in Chapter III. It has been proved that cellular capillaries which are neither straight nor of uniform diameter can be replaced by a single capillary having a diameter equal to the mean diameter of all the capillaries operating. Thus r in e-

quation (A), which may be termed equivalent radius, may be determined by measuring h with a liquid which is known to wet the powder completely (θ = zero). Measurement of h with the capillarimeter has already been explained. It has been shown that the capillary height of a liquid in the interstices of sand or soil equals the pressure deficiency against which the liquid can be held in the interstices.

TABLE 40. Contact angles of various liquids with sands of different grades.

Mean diameter of sand particles (mm)	Contact angle with		
	Alcohol	Kerosine	Capillary pull in water (h) (cm)
0.58	0	0	17
0.417	0	0	24
0.385	0	0	26
0.303	0	17° 50'	33
0.286	0	21° 0'	35
0.217	0	31° 46'	46
0.184	19° 36'	25° 48'	54.3
0.160	31° 42'	38° 12'	62.5
0.104	21° 12'	31° 54'	96

TABLE 41. Contact angles of various liquids with silica of different grades.

Description	Capillary height cm	Contact angle	
		Kerosine oil	Alcohol
Freshly precipitated	37	53° 48'	34° 6'
Ground in pestle and moisture for one hour	59.3	64° 54'	35° 36'
Ground in a colloid mill for one hour	75	57° 42'	60° 48'
Ground in a colloid	120	61° 6'	56° 18'

In the first instance the angle of contact was measured with sands of different grades, as well as ground and unground silica, using alcohol and kerosine as the contacting liquids. The results are given in Tables 40 and 41.

It will be seen that contact angle depends not only on the nature of the liquid but on the size of particles. The results are plotted in Figure 46, from which it is clear that there is perhaps a critical diameter of particles below which the contact angle assumes a finite value. There is, however, no correlation between the size of particles and the contact angle beyond a vague indication that with

decreasing diameter the value of the contact angle increases. It is, however, not unlikely that there may be several maxima and minima. In any case the relation is much more complex than might appear at the surface.

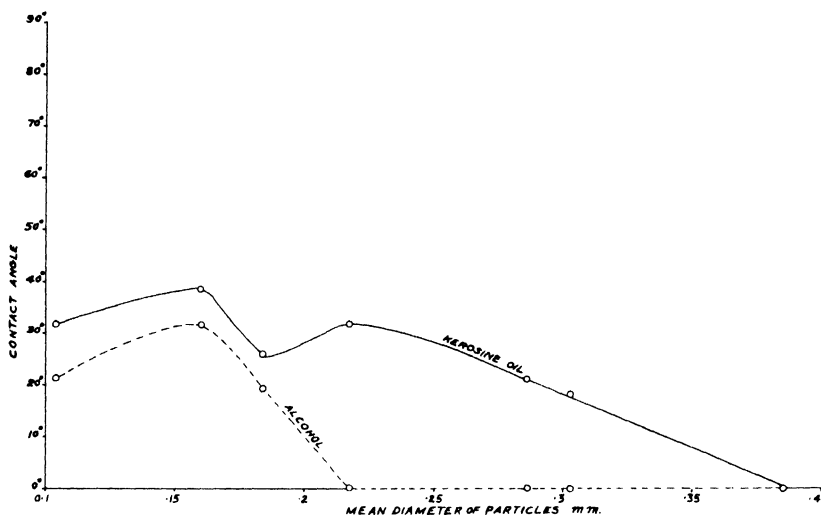



Fig. 46. Relation Between Contact Angle and Size of Particles

TABLE 42. Heat of wetting, contact angles and densities of silica with different liquids.

Liquid	Heat of wetting (calories per 100gm.)	Contact angle
Water	18.2	0
Benzene	16.5	9° 36'
Kerosine oil	8.25	53° 48'
Alcohol	15.9	34° 6'
Acetone	16.9	0
Glycerine	15.7	26° 42'

These results are very important in explaining the lower heat of wetting obtained with certain liquids as compared to water. Obviously in such cases the liquid is unable to enter the finest capillaries, or there is imperfect wetting. This will be clear from Table 42, in which are given the heat of wetting for dry silica with respect to various liquids along with the contact angles. It is clear that when the contact angle is high, causing imperfect wetting of the capillaries, the heat of wetting is low. The results, however, are not capable of any quantitative interpretation for obvious reasons.

The fact that contact angle for the same substance depends on particle size is of far-reaching consequence. It offers at least a

qualitative explanation of the well known differences in the moisture absorption and heat of wetting of the same substance with respect to various liquids. It also explains the possible effect of "activation" on adsorption, which may consist only in the alteration of the contact angle. It may throw light on curiously shaped adsorption isotherms which do not fit any theory or equation.

It is true that the explanation is of an omnipotent character, and as such may be called an admission of ignorance of the laws of adsorption. It must be admitted, however, that any explanation of adsorption based on residual valencies and mono- or polymolecular layers would hardly account for such enormous differences in the nature of adsorption, even in its qualitative aspects. Variations in the contact angle, on the other hand, are capable of experimental demonstration, and it is no strain on the imagination to suppose that these variations play a decisive role in determining the nature and extent of adsorption.

As pointed out above, the results so far obtained are capable of only qualitative interpretation; measurements of contact angle cannot be carried out on particles finer than 0.05 mm diameter, and in actual absorbents we are dealing with much finer particles. It is significant that in an attempt to correlate the physico-chemical properties of the activated earths with their decolorizing property for oils, it was found that the finest particles were inert in this respect. This was attributed to the impossibility of the oil's entering the finest pores. Such a result is easily comprehensible in the light of what has been said in the foregoing. namely an increase in the value of the contact angle as the particle size decreases.

Contact Angle of Water with Organic Compounds

Water is known to form contact angles up to 105° with organic compounds; greater angles than this have not been established with certainty. Adam and Jessop have used contact angles to explore molecular orientation at solid surfaces. Working with long-chain acids and alcohols they showed that the outer surface of these consist of hydrocarbons when solidified naturally; the contact angles had high values and were the same in every case.

If a cut was taken with a knife through the solidified mass, the contact angles of the surfaces so exposed proved to be variable. This was attributed to the fact that cutting through the interior exposed a variable number of water-attracting groups. The variation in the results on the cut surfaces of the acids and alcohols is in perfect accord with the crystal structure of these substances; and the character of the cut surface depends on the direction which the knife takes relative to the sheets of molecules which constitute the crystal. If it travels parallel to these sheets, it will pass between them, exposing only hydrocarbon groups, so that the contact angle will be about 105°; if it travels perpendicular to them, one water-attracting group will be exposed for each molecule, or every fifteen CH_2 or CH_3 groups.

It is also noticed that only a small proportion of active water-attracting groups is sufficient to effect a great increase in the attractive power for water. These measurements of contact angle were made on these substances in the form of sheets, and all attempts to obtain a surface with all the water-attracting groups oriented outward by crystallizing them on a water surface failed. Not only do powders present a larger surface, but it is possible to prepare oriented surfaces in that case. For instance, stearic acid can be obtained with all its carboxyl groups on the surface by precipitating it from an alcoholic solution added in a thin stream to water under violent agitation. Similar results are obtained if an emulsion of molten stearic acid in water kept above its melting point is slowly allowed to cool. The emulsion is kept violently stirred during cooling to prevent the particles from coalescing. The stearic acid prepared by either of the two methods is capable of being titrated by alkalies in the cold, using phenolphthalein as indicator. Evidently in this case all the water-attracting carboxyl groups are on the surface.

TABLE 43. Contact angles of water with stearic acid prepared in different ways.

Stearic Acid sample	Capillary height with alcohol (cm)	Contact angle	
		Well soaked	Water freshly sprinkled
A	12.5	45° 15'	--
B	12.5	41° 24'	58° 0'
C	33.0	50° 12'	81° 30'
D	43.0	44° 51'	82° 40'

It was of interest to compare organic compounds in the form of powders prepared in different ways to study the influence of polar groups on contact angle.. The various compounds are discussed under their appropriate headings.

Stearic acid:

The following samples of stearic acid were examined:

A: Ordinary commercial stearic acid (65°C: iodine value, 3-6)
B: Stearic acid crystallized from benzene under violent stirring.
C: Stearic acid crystallized from alcohol under violent stirring.
D: Stearic acid obtained by cooling a hot emulsion in water under violent stirring.

The contact angle of each was determined by using alcohol as the liquid, giving zero angle. The contact angles with water in the case of different samples are given in Table 43.

It will be seen that when the stearic acid is well soaked there is not much difference in the contact angles of the various samples. However, when the soaking is not complete, not only has the con-

tact angle a higher value, but the difference between individual samples is much greater. This is evidently due to locked-in air, and the results have no more significance than pointing out the desirability of thorough soaking before determining contact angles. In view of the slight differences in the contact angles of the various samples, it is evident that the orientation of the molecules on the surface of the solid has very little effect on the contact angle in this case.

In the experiments detailed above there is one snag which is worthy of note. The size distribution of particles in the various samples of stearic acid may not be the same. As we know that contact angle is influenced by particle size, a comparison of the results is likely to be erroneous unless we know the average diameters of particles in each case. As a matter of fact, this was actually determined with alcohol, which is assumed to give zero contact angle; but the values are by no means the same in every case, as will be seen from Table 43, in which these values are included. However, unless we know the relation between the mean diameter of the particles and the contact angle in every case we can not very well put down the variations, if any, as due entirely to orientation of the molecules on the surface.

TABLE 44. Contact angles of water with fatty acids deposited on sand particles (.59 mm and .28 mm diameter).

Compound	Contact angle		Standard values
	.59 mm	.28 mm	
Stearic acid	49° 44'	55° 12'	53
Palmitic acid	50° 34'	54° 6'	54
Myristic acid	62° 0'	55° 54'	60

An attempt was made to overcome this difficulty by depositing stearic acid on sand particles directly in the molten state. The sand chosen had a mean diameter of 0.28 mm. One percent of stearic acid on the weight of the sand was deposited which was well stirred during deposition, to insure a uniform film. The size of sand particles was particularly chosen in the coarser range in which influence of particle size on contact angle is not apparent.

The simplicity of technique for measuring contact angles of stearic acid with respect to water by depositing it on the sand particles justified its adoption in the case of other fatty acids. In Table 44, are given values of contact angles for the three common acids.

Angle of Contact of Charcoal in Different Liquids

Assuming the contact angle of charcoal in alcohol to be zero, its value was determined in the case of water and acetone. The charcoal was passed through a 60-mesh screen, and readings were taken both with the portion passing through and that retained. The

TABLE 45. Contact angle of charcoal with water and acetone assuming 0 angle with alcohol.

Liquid	Contact angle	
	Activated	Unactivated
Charcoal passing 60 mesh		
Water	53° 6'	52° 6'
Acetone	0°	0°
Charcoal retained on 60 mesh sieve		
Water		9° 6'
Acetone		0°

results are given in Table 45. The values for contact angles of charcoal in different liquids are in agreement with the absorption values for these liquids from the vapor phase.

CHAPTER X

ABSORPTION OF VAPORS FROM ORGANIC LIQUIDS

From the general relationship $pF = 6.5 - \log_{10} (2 - \log_{10} h)$, it has been shown that it is possible to calculate the diameter of the capillaries in which water may be held in an atmosphere of a particular relative humidity, h, since $pF = -\log D$, where D is the diameter of the particles in the interstices of which the capillary of a particular diameter is found. This relationship has been used for finding the size distribution of particles in soils.

Since the thermodynamic relationship is quite general, it should be capable of being verified in the case of liquids other than water. Hence from a knowledge of the surface tension of organic liquids and the negative pressure to which they would be subject if held in a capillary of a particular diameter, it should be possible to calculate from the ultra-mechanical analysis of a soil, the relationship between relative humidity and the absorption of vapor from any liquid for which the usual physical constants are known. The calculated values could then be verified experimentally and the truth of the capillary hypothesis established.

The following organic liquids were used for the purpose: (1) methyl alcohol, (2) ethyl alcohol, (3) acetone, (4) ether, (5) benzene.

Tables 46 to 50 give the relative humidities of the various liquids when mixed with different amounts of vaporless liquids or solids. These values have been taken from "International Critical Tables", but since their presentation in this form involved a good deal of calculation, they are given here to facilitate reference by other workers.

From the relationship between pF (or size of particles, since $pF = -\log D$) and relative humidity, the relation between the pF of particles of various sizes and the corresponding values of relative humidities for water as well as other organic liquids were calculated, and are given in Table 51.

It will be seen from Table 51 that there is a large difference between the relative humidities for organic liquids and that of the water, though this difference is not so striking in the case of pF values, the latter being on the logarithmic scale. These differences also narrow down with the increase in relative humidity and almost vanish near the saturation point. Taking a particular case,

TABLE 46. Relative humidities of ethyl alcohol-glycerol mixtures.

% Mol. conc. of glycerol in ethyl alcohol	% by volume of glycerol in alcohol-glycerol misture	Relative humidity
20	23.9	91.2%
50	55.7	76.31%
80	83.4	46.56%
90	91.9	28.14%

TABLE 47. Relative humidities of Acetone Oleic acid mixtures.

Mol. % of Oleic acid	% of oleic acid by volume in the mixture	Relative humidity
40	76.2	67.5
60	87.8	47.8
90	97.7	14.5

TABLE 48. Relative humidities of ether-sulphuric acid mixtures.

Mol. % of sulphuric acid	% of sulphuric acid by volume in the mixture	Relative humidity
2	0.94	98.58
19	10.6	85.58
37	22.9	35.25
39	24.4	29.02
52	35.4	4.32

TABLE 49. Relative humidities of methyl alcohol-glycerine mixtures.

Mol. % of glycerine	% of glycerine by volume in the mixture	Relative humidity
6	12.05	95.10
22	34.02	86.74
37	51.6	77.10
50	64.5	65.30
60	73.2	54.22
80	87.9	31.1
85	91.2	24.1

TABLE 50. Relative humidities of Benzene-naphthalene mixtures.

Mol. % of naphthalene	% of naphthalene by weight in the mixture	Relative humidity
9	13.9	91.26

the capillaries responsible for the absorption of moisture at 10% relative humidity, when filled to the same extent with ethyl alcohol, will give a relative humidity of 41.68%. Therefore, from an atmosphere of 41.68% relative vapor pressure of alcohol, a soil would take up alcohol vapors just enough to fill the capillaries formed in the interstices of particles of a limiting diameter of $10^{-6.5}$ cm. Similar remarks would apply in the case of other liquids.

TABLE 51. pF of particles of various sizes in water and various organic liquids and the corresponding values of relative humidity.

Particle size (cm)	pF values for					Percentage Humidity				
	Water	Ethyl alcohol	Acetone	Methyl alcohol	Benzene	Water	Ethyl alcohol	Acetone	Methyl alcohol	Benzene
10^{-4}	4.0	3.5798	3.5658	3.5899	3.6539	99.5	99.72	99.68	99.70	99.62
$10^{-4.2}$	4.2	3.7798	3.7659	3.7907	3.8533	98.8	99.55	99.50	99.54	99.47
$10^{-4.6}$	4.6	4.218	4.1659	4.1901	4.2198	97.1	88.8	99.17	98.88	98.70
$10^{-5.0}$	5.0	4.5798	4.5658	4.5899	4.6539	92.96	97.27	97.36	97.21	96.77
$10^{-5.2}$	5.2	4.7798	4.7659	4.7907	4.8533	89.08	95.52	95.84	95.61	94.93
$10^{-5.4}$	5.4	4.9797	4.9659	4.9900	5.0531	83.3	93.28	93.51	93.13	92.10
$10^{-5.6}$	5.6	5.218	5.1659	5.1901	5.2198	74.8	88.65	89.86	89.33	87.78
$10^{-6.0}$	6.0	5.5798	5.5658	5.5899	5.6539	48.3	75.85	76.33	75.34	72.02
$10^{-6.2}$	6.2	5.7798	5.7659	5.7907	5.8533	31.5	63.84	65.30	63.78	59.47
$10^{-6.5}$	6.5	6.0799	6.0656	6.0899	6.1532	10.0	41.68	42.87	41.78	36.03

TABLE 52. Single value constants of soils used in vapor absorption studies.

Soil No.	% clay (.002 mm)	% ultra-clay (.0001 mm)	Exchangeable		pH
			Ca	Na+K	
P.C. 13	59.2	45.8	55.6	3.3	8.53
P.C. 72	45.9	11.4	14.0	1.8	8.30
P.C.111	8.4	4.6	9.2	Nil	7.93
P.C.123	85.5	30.2	12.0	17.4	8.92
P.C.246	46.4	12.6	23.2	0.8	7.20
P.C.172	52.5	18.2	24.0	4.4	8.50
P.C.173	39.7	9.7	21.4	2.0	8.35
P.C.175	25.4	7.7	10.4	1.6	7.88

Eight soils were used for the purpose as representative of capillary systems of diverse character. They were chosen from a large collection to give the maximum variations in their physico-chemical characteristics. Some of the important single-value constants of the soils are given in Table 52. Moisture absorption of various soils from atmospheres of different humidities are given in Table 53.

Values given in Table 51 enable us to calculate the percentage saturation of vapors of any liquid mentioned therein from the corresponding value of relative humidity of water. If the relative humidities of water vapors are plotted against the percentage satur-

ation of vapors for the various liquids studied, smooth curves are obtained in every case which enable intermediate values to be interpolated. It is presumed that since at the corresponding values of percentage saturation of vapors, the same capillaries would be involved, the volume of the liquid absorbed would be the same.

TABLE 53. Moisture absorption of various soils from atmosphere of different humidities.

Soil No.	% moisture absorbed from different humidities						
	10%	30%	50%	70%	90%	96%	99%
13	4.1	7.34	8.59	11.07	12.89	14.09	16.79
72	0.60	1.2	2.01	2.45	4.07	4.51	6.43
111	0.23	0.59	0.59	0.82	1.66	2.11	2.32
123	2.0	3.31	4.35	7.25	10.63	11.06	14.32
246	1.19	2.79	2.66	4.00	6.08	7.07	7.90
172	2.62	4.36	5.17	6.86	8.34	8.62	10.84
173	0.51	1.51	1.54	2.31	2.88	3.18	4.90
175	0.34	0.86	1.19	1.88	2.01	2.73	3.96

TABLE 54. Volume of ethyl alcohol absorbed from atmospheres of different humidities by soils.

Soil No. P.C.	Det'd or Calc	Volume absorbed in cc. per 100 gm soil from atmospheres of different humidities					
		28%	46%	73%	83.4%	87%	92%
13	Det'd	4.6	5.75	8.82	10.1	10.45	12.2
	Calc	2.0	4.7	8.2	10.15	11.2	12.25
72	Det'd	1.5	2.5	3.10	4.97	5.03	6.8
	Calc	0.30	0.8	1.6	2.0	2.65	3.45
123	Det'd	2.26	3.3	5.45	4.61	6.01	9.17
	Calc	1.02	1.25	4.0	6.0	7.55	9.4
246	Det'd	1.56	2.3	3.46	4.39	4.64	5.75
	Calc	0.6	1.5	2.7	3.7	4.20	5.30
172	Det'd	1.71	3.16	4.66	5.72	5.60	7.41
	Calc	1.4	3.0	4.92	6.2	7.06	7.75
173	Det'd	0.44	0.56	1.31	2.05	2.12	3.82
	Calc	0.26	0.68	1.50	2.0	2.4	2.7
175	Det'd	0.32	0.50	0.90	2.21	2.37	3.22
	Calc	0.17	0.44	1.04	1.6	1.87	1.95

From this simple deduction the absorption of vapors of any liquid at various values of percentage saturation could be calculated when this relation is known in the case of water.

In Tables 54 to 57 the calculated as well as the experimentally determined values of the volumes of different liquids absorbed by

100 grams of soil from atmospheres of different humidities are given. The observed values were obtained by placing soils in atmospheres of different vapor pressures of various liquids. The ratios in which these liquids were mixed with other substances to lower their vapor pressures to different extents are given in Tables 46 to 50. The calculated values are nothing but moisture absorption

TABLE 55. Volume of acetone absorbed from atmospheres of different humidities by soils.

Soil No. P.C.	Volume (cc) absorbed by 100 g of soil from atmospheres of different degrees of saturation					
	14.5%		47.8%		67.5%	
	Obs	Calc	Obs	Calc	Obs	Calc
13	3.46	1.0	4.0	4.7	8.84	7.7
72	2.51	0.2	2.51	1.5	2.65	1.8
111	0.44	0.7	0.6	0.31	0.50	0.6
123	2.87	0.5	2.9	1.25	5.0	3.83
246	2.68	0.3	2.9	1.5	4.29	2.60
172	3.00	0.6	3.2	3.0	4.60	4.56
173	0.8	0.15	1.0	0.68	0.85	1.5
175	0.96	0.10	0.9	0.44	1.08	0.9

TABLE 56. Volume of benzene absorbed from atmospheres of different humidities by soils.

Soil No. P.C.	Volume (cc) absorbed by 100 g of soil at 92% humidity	
	Observed	Calculated
13	9.3	12.4
72	3.9	3.8
111	0.8	1.4
123	11.0	9.8
246	4.8	5.4
172	5.4	7.9
173	2.2	2.4
175	1.6	1.86

TABLE 57. Volume of methyl alcohol absorbed from atmospheres of different humidities.

Soil No. P.C.	Volume (cc) absorbed by 100 g of soil from atmospheres of different degrees of saturation											
	24.1%		31.1%		54.2%		77%		86.7%		95.1%	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
13	3.7	1.5	4.0	2.6	7.3	5.9	11.2	8.8	12.1	11.2	13.5	12.9
72	1.3	0.2	1.4	0.3	2.7	1.15	3.0	2.4	3.8	2.55	4.6	3.9
111	0.25	0.15	0.4	0.2	0.5	0.5	0.67	0.62	0.7	0.9	0.8	1.6
123	2.2	0.7	2.3	0.9	3.4	2.1	4.4	4.4	6.2	7.7	11.2	10.5
172	1.8	1.0	2.0	1.75	2.5	3.6	3.4	5.2	3.9	6.94	4.8	8.2
173	0.58	0.15	0.7	0.25	0.8	1.05	1.7	1.6	1.9	2.3	2.1	2.8
175	0.57	0.1	0.7	0.15	0.95	0.65	1.3	1.15	2.3	1.82	2.7	2.1
246	2.2	0.45	2.2	0.75	2.9	2.25	3.6	3.5	4.1	4.1	5.0	5.8

by soils at humidities corresponding to the given percentage saturation in the case of a particular liquid. It is assumed that, since the same size of capillaries is involved at the corresponding values of relative humidities, the volume of the absorbed liquid must be the same, irrespective of the nature of the liquid. The percentage by volume was calculated from the density of the liquid in every case. It must be admitted that some error would be involved, especially at low humidities, from the fact that the liquid held in the minute capillaries may be compressed and its density may not be the same as at atmospheric pressure.

In the calculation of these volumes, however, no allowance was made for the compressibility of the various liquids, partly because the magnitude of the correction would be very small, and considering the nature of substances involved it would be superfluous to consider such correction factors in view of the experimental errors involved.

TABLE 58. Amount of water held as monomolecular layer on the surface of soils.

Soil No. P.C.	Water as monomolecular layer calculated from soil surface (%)
13	1.656
72	0.38
111	0.07
123	0.98
246	0.49
172	0.71
173	0.27
175	0.20

From the perusal of the results given in Tables 54 to 57 it will be seen that the agreement between observed and calculated values in the case of all the liquids is sufficiently close to prove the soundness of the capillary hypothesis. At very low humidities, the agreement is not so good, but when it is remembered that a relative vapor pressure of 29.02% in the case of ether, for instance, corresponds to a relative humidity of 2.5% for water, a larger magnitude of error becomes comprehensible.

It is not unlikely that apart from the capillary moisture a certain amount of moisture might exist as a monomolecular layer held to the surface by chemical forces. The amount of water thus held could be calculated from the specific surface of these soils. These calculated values are recorded in Table 58.

The magnitude of these values indicates that they are of the order of moisture absorption at about 5% humidity (c.f. Table 53). From the nature of the moisture content-relative humidity curve it is seen that the portion of the curve up to 10% humidity is relatively less steep, and resembles that of a salt hydrate where a change of moisture produces no change in the vapor pressure until the entire

water corresponding to a particular hydrate is driven out. This suggests that a part of the water corresponding to the monomolecular layer may be chemically held. Since the loss of this part of the water would produce no change in the vapor pressure its superimposition on the loss of the capillary water would result in a vapor-pressure curve that is less steep in this region. It is also likely that when capillaries reach molecular dimensions, the thickness of the adsorbed layer would begin to tell on the size of the capillaries, which would appear smaller than they actually are. If vapors of organic liquids do not form a monomolecular chemically held layer it is conceivable that the smallest capillaries would hold

TABLE 59. Absorption of organic vapors by various charcoals.

Relative humidity (%)	Coconut		Pistachio nut		Coconut husk	
	Unactivated	Activated	Unactivated	Activated	Unactivated	Activated
			A. Ethyl Alcohol (%)			
28.14	3.02	12.03	7.1	8.3	6.8	8.1
46.56	9.18	11.5	8.05	8.9	8.2	8.9
76.31	12.02	14.7	9.43	10.7	8.0	9.9
91.20	12.28	13.7	13.45	12.7	7.96	11.3
			B. Methyl Alcohol (%)			
24.1	7.62	10.54	1.84	5.88	2.25	8.17
31.1	8.2	10.9	3.76	6.40	5.69	9.88
54.2	8.83	11.03	4.2	-	6.89	8.75
65.3	10.1	12.52	7.9	9.14	9.29	10.35
77.1	10.78	12.4	7.95	9.97	9.59	10.69
86.74	11.6	14.7	10.42	12.05	9.59	11.38
95.1	11.57	12.9	13.5	-	-	-
			C. Acetone (%)			
14.5	12.1	10.69	5.83	8.17	10.1	10.78
47.8	12.98	13.70	9.15	10.4	11.06	12.46
67.5	13.12	12.88	10.3	11.33	10.15	14.0

larger quantities of these liquids which would be subject to capillary laws, and there would be a greater discrepancy between the calculated and found values in this region.

Absorbent charcoal has the peculiar property of being more easily wetted by organic liquids than by water. It was therefore, considered advisible to include charcoal in these studies.

The results of absorption of various organic liquids by coconut shell, coconut husk and pistachio nut charcoal, activated as well as unactivated, are given in Table 59. From these results the values of different liquids absorbed at equivalent humidities were interpolated. The data, expressed as volumes of different liquids absorbed at equivalent humidities, are given in Table 60. These val-

ues should be equal according to the capillary condensation theory, provided the contact angle of charcoal is the same in all these liquids. The results (Table 60) show fairly good agreement in the case of absorption of organic liquids, particularly when the samples are activated. In the unactivated samples, differences are perhaps

TABLE 60. Absorption of different liquids from vapor phase on charcoals at equivalent humidities.

Equivalent relative humidity of water (%)	cc of liquid absorbed by samples of charcoal							
	Unactivated coconut				Activated coconut			
	Water	CH_3OH	C_2H_5OH	CH_3COCH_3	Water	CH_3OH	C_2H_5OH	CH_3COCH_3
5.0	1.1	9.52	3.6	15.5	1.4	13.2	14.8	14.6
10.0	10.0	10.62	11.2	16.0	2.1	13.6	14.4	16.2
31.5	4.4	12.62	13.7	16.4	4.8	15.5	16.2	16.0
48.3	5.0	13.47	15.0		8.6	15.5	18.0	
74.8	8.1	14.5	15.1		13.4	16.1	18.1	
84.0	11.0	14.5	15.5		16.8	16.1	17.2	
	Unactivated coconut husk				Activated coconut husk			
5.0	0.75	2.8	8.25	13.1	0.9	10.2	10.5	14.3
10.0	1.59	7.25	10.0	13.5	1.66	11.2	11.0	15.0
31.5	2.4	11.6	10.0	13.1	15.00	12.9	11.8	16.8
48.3	5.9	11.6	10.0		9.13	13.3	12.4	
74.8	11.9	12.1	10.0		12.2	14.2	13.7	
84.0		11.1	10.0			13.5	14.6	
	Unactivated pistachio nut				Activated pistachio nut			
5.0	0.7	5.0	9.4	10.1	1.8	8.4	10.7	11.9
10.0	3.47	5.2	10.0	10.6	3.49	9.5	11.1	12.6
31.5	3.54	9.8	11.3	12.5	3.92	11.5	12.6	14.4
48.3	3.66	10.1	12.2		4.28	12.5	13.5	
74.8	5.62	13.4	16.1		7.3	14.3	15.7	
84.0	9.0	14.5	17.7		9.6	14.9	16.6	

to be expected, especially at lower humidities, because the surface is less clean and, therefore, the contact angle does not have the same value in all the liquids.

The results of moisture absorption present some interesting features. At lower humidities water is absorbed to a very small extent, but with increase in humidity the values approach those observed for other liquids. The explanation of this deviation very probably lies in the fact that some of the finest capillaries closely concerned in moisture absorption at lower humidities are not properly wetted by water because of the finite value of the contact angle. This was verified by measuring the contact angle of a sample of charcoal in water and acetone, assuming it to be zero in the case of ethyl alcohol. The results showed that while its value was zero for acetone, it was 9 to 53° for water, depending on the size of charcoal particles.

CHAPTER XI

HEAT OF WETTING

When a dry soil is brought into contact with water or other liquids, there is a considerable rise of temperature, due to heat of wetting. This phenomenon is of general occurrence, as practically all substances possessing a capillary structure capable of absorbing liquids or gases show a definite heat of sorption. The exact mechanism of this exothermic reaction is not known, but the production of heat may be due to the compression of the liquid consequent on its absorption in the minute capillaries, or it may even be due to the chemical action between the sorbing surface and the sorbed liquid. Obviously this phenomenon is capable of throwing a good deal of light on the mechanism of moisture absorption by capillary systems, for by a process of elimination it would be possible to decide whether the forces involved are chemical or purely physical in nature. The question is of great importance not only in soils, but for all substances possessing a capillary structure.

The heat of wetting of soils has been measured by several workers, but the measurements have been confined chiefly to the total heat of wetting. Very little is known about the heat of wetting when soil is allowed to absorb increasing amounts of water. It seems reasonable to suppose that the greatest heat of wetting will be produced in the initial stages, and that it will gradually become less as the soil takes more and more water.

The difficulty of measuring heat of wetting with gradual increments of moisture is very great. For uniformity of results, the absorption must be allowed to take place in the vapor phase, and it is not possible to measure the rise of temperature accompanying the slow absorption of moisture. The heat of wetting can, however, be measured in an indirect way, as follows: Weighed amounts of a soil are brought to equilibrium with different humidities and consequently made to take up definite but varying amounts of moisture. Heat of wetting is then measured in every case. The difference in the heat of wetting between the dry and the moist soil is taken as that due to the initial moisture content.

Sulphuric acid-water mixtures were used for controlling the humidities. Heat of wetting was measured in a Dewar Cylinder with

a Beckmann thermometer. Approximately 5 grams of soils were added to 50 cc of water. Heat of wetting in calories per gram of soil, Q, was calculated from the following formula:

$$Q = \frac{1}{p}\left\{(p + q)\ s + w\right\}\ (T-T')$$

where p is the weight of the dry soil, q the weight of the liquid, s the specific heat of the soil suspension, w the water equivalent of

TABLE 61. Heat of wetting in calories per gram soil at different humidities.

Soil No. P.C.	Relative humidity					
	0%	10%	30%	50%	70%	90%
13	10.9	4.004	2.76	1.87	0.7305	0.465
72	4.75	1.95	1.56	1.05	0.54	0.112
111	1.43	1.09	0.725	0.453	0.234	0.06
123	5.48	3.318	2.29	1.45	0.793	0.322
246	6.65	2.488	1.81	0.977	0.613	0.246
172	7.625	3.033	1.896	1.293	0.443	0.277
173	3.80	1.82	1.57	0.68	0.240	0.118
175	2.98	2.25	1.57	0.494	0.226	0.112

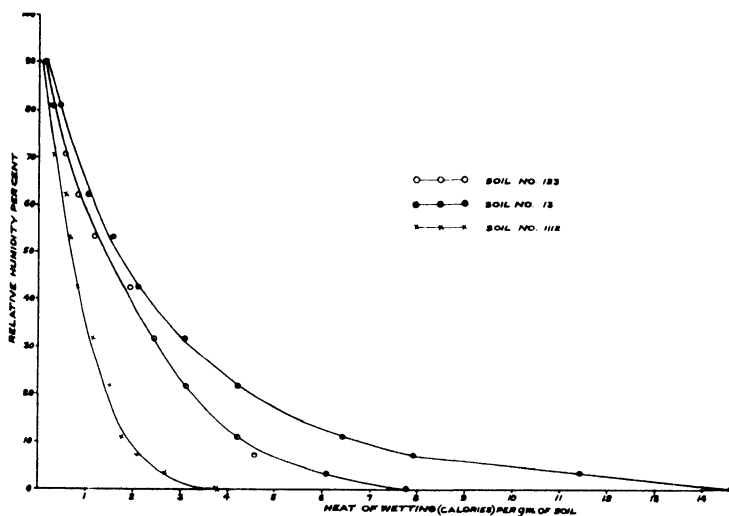



Fig. 47. Relation Between Heat of Wetting and Relative Humidity of Soil

the calorimeter, thermometer, stirrer, etc., T_0 the initial temperature of soil and the liquid, and T_1 the final temperature of the suspension. The results are given in Table 61 and plotted in Fig. 47 in the case of a few typical soils.

From these results the heat of wetting per gram of water absorbed between different humidity intervals is calculated for each soil. It is assumed that since the same size of capillaries is involved in moisture absorption between any two humidities, the heat

of wetting is the same. It must be remembered, however, that this will be strictly true if the size distribution of particles governed by the two humidities is the same, *i.e.*, if the slope of the summation curves in the two cases is the same. It is presumed that slight variations may be smoothed out by taking small humidity intervals.

The values were calculated as follows: The heat of wetting for any humidity interval was interpolated from the curve (Fig. 47). The moisture absorption for the interval was then interpolated from the corresponding vapor pressure-moisture content curve of the soil and the results calculated for a gram of water absorbed by 100 grams of soil in each case. These values are given in Table 62.

TABLE 62. Heat of wetting in calories per gm of water absorbed between different intervals of relative humidity.

Soil No. P.C.	Relative humidity									
	0-10 %	10-20 %	20-30 %	30-40 %	40-50 %	50-60 %	60-70 %	70-80 %	80-90 %	90-100 %
13	1.7	0.4	0.4	0.65	0.73	0.50	0.44	0.13	0.15	0.12
72	*4.7	0.24	0.2	0.65		0.45	0.40	0.27	0.26	0.05
111	1.5	1.0	1.0			1.0	0.90	0.20	0.22	0.09
123	1.65	0.4	0.4	0.80	0.80	0.22	0.23	0.13	0.15	0.09
246	3.46	0.4	0.43			0.26	0.30	0.19	0.17	0.13
172	1.76	0.6	0.7	0.75	0.7	0.55	0.51	0.11	0.12	0.11
173	*4.00	0.24	0.26			0.70	0.60	0.20	0.20	0.06
Mean	1.65	0.47	0.48	0.71	0.74	0.52	0.48	0.18	0.18	0.09

* These values were not included in calculating the averages.

The heat of wetting of a number of soils was calculated from their vapor pressure-moisture absorption curves, taking the average values of heat of wetting at different humidity intervals as given in Table 62. These values were then compared with those determined experimentally, and are given in Table 63, from which it will be seen that the agreement between the calculated and determined values is as close as could be expected from the nature of a material like soil. These results constitute strong evidence in favor of the purely physical nature of moisture absorption.

In order to see if the general relationship between heat of wetting and moisture absorption at various humidities was applicable to other liquids, a number of soils were brought into equilibrium with alcohol-glycerin and acetone-oleic acid mixtures of different vapor pressures and the heat of wetting determined. (Tables 64 and 65). These results when plotted give smooth curves similar to those obtained with water. There appears to be a constant difference between heat of wetting with alcohol and water (with dry soil). This may be due to a difference in the heat of compression.

Heat of Wetting in Various Organic Liquids

The heat of wetting of these eight soils in a number of organic liquids was determined. It was found that its value in water, methyl

alcohol, ethyl alcohol and amyl alcohol is of the same order in individual soils. In the case of glycerol, which contains three CH-groups, the value is much less in soils P.C. 13, 72 and bentonite; but the difference is not large in other soils. When heat of wetting in ethyl acetate, a liquid also containing a polar group, is considered, the case is similar. It appears that when the number or size of the polar groups is large and the size of the capillary pore is

TABLE 63. Comparison of calculated and determined values of heat of wetting of soils in water.

Soil No. P.C.	Heat of wetting in calories per gram of soil		Soil No. P.C.	Heat of wetting in calories per gram of soil	
	Calc	Det'd		Calc	Det'd
15	4.66	4.50	83	1.92	2.43
16	0.51	0.47	85	4.28	3.09
17	1.25	0.97	86	4.97	5.19
18	2.37	2.76	89	1.41	2.51
19	7.02	7.72	90	2.37	1.59
20	0.97	0.976	91	2.03	3.06
38	11.38	13.40	92	2.36	2.64
47	1.39	1.30	93	2.18	1.24
51	0.90	1.05	94	2.62	2.70
64	2.004	0.75	97	2.26	2.21
67	1.30	0.94	98	1.65	2.27
70	3.32	1.82	99	1.64	0.70
71	3.14	1.66	100	1.11	1.19
88	3.56	1.62	96	2.35	1.33
133	0.85	0.65	101	1.06	0.995
161	7.99	4.76	102	1.79	0.98
129	3.65	3.06	104	2.17	1.31
146	15.33	14.09	105	2.25	1.54
261	5.16	4.32	106	2.73	3.16
63	0.77	0.99	107	2.71	0.91
65	0.53	0.93	109	1.12	1.41
66	1.54	2.37	110	0.63	0.89
68	1.42	3.55	112	1.94	1.14
69	1.20	0.85	113	0.93	1.29
73	2.99	3.26	114	2.17	2.17
74	2.55	2.91	118	2.73	1.01
76	6.83	8.89	121	1.78	2.47
77	2.70	3.11	122	1.58	2.05
78	2.98	3.17	124	2.75	1.46
79	1.78	4.73	126	3.04	1.29
80	0.916	1.00	127	2.65	2.68
81	6.48	11.5	145	9.61	9.00
82	5.03	6.20			

small in a soil (as in P.C. 13 and bentonite, which are mostly colloidal) proper wetting does not take place. The values for heats of wetting for benzene, chloroform and acetone also are less than for water, the maximum difference being noted in the case of P.C. 13 soil and bentonite. This shows that liquids containing no polar groups can be absorbed less effectively in the interstices between the soil particles, and the smaller these pores in a soil the less

effective the absorption. Also, if the size of the molecules of the absorbed liquid is large, as in the case of paraffin liquid and kerosine oil, there is a further decrease in the value of the heat of wetting in all soils. It is presumed that these long-chain molecules cannot properly enter the interstices, which are almost down to the size of molecules. A finite value of contact angle is another factor in the failure of some of the organic liquids to enter capillaries below a certain limiting size.

TABLE 64. Heat of wetting (calories per gram soil) in alcohol after allowing the soil to come to equilibrium with alcohol-glycerine mixtures of different vapor pressures.

Soil No. P.C.	Heat of wetting at different relative humidities				
	0%	28%	46%	73%	91%
13	10.0	2.32	1.7	0.986	0.222
72	3.7	0.800	0.729	0.238	0.058
111	1.01	0.325	0.242	0.239	0.028
123	4.38	1.13	0.865	0.440	0.284
246	4.82	0.91	1.05	0.319	0.260
172	6.07	1.12	1.12	0.318	0.284
173	2.70	0.684	0.398	0.089	0.0575
175	2.37	0.486	0.595	0.119	0.0287

TABLE 65. Heat of wetting (calories per gram soil) in acetone after bringing into equilibrium with different vapor pressures of acetone from acetone-oleic acid mixtures.

Soil No. P.C.	Heat of wetting at different vapor pressures			
	0%	14.5%	47.8%	67.5%
13	7.72	1.53	1.44	0.961
72	2.41	0.82	0.66	0.573
111	1.00	0.53	0.21	0.211
123	4.05	1.25	1.24	0.657
246	4.02	1.10	1.00	0.72
172	4.75	1.27	1.25	0.737
173	1.21	0.62	0.55	0.243
175	0.86	0.47	0.405	0.27

Density of Soils in Various Liquids

If heat of wetting is due to the absorption of liquids in the micropores of soil particles, and if various liquids give different values for heat of wetting because of the difference in their ability to enter and fill completely capillaries of various sizes, then it is plausible that the values for the densities of soils determined in various liquids will differ. If, for instance, a liquid cannot properly fill all the interstices in a soil, the weight of that liquid displaced by the soil will be comparatively greater, and consequently the density will be less in such a liquid. To verify this contention, the densities of a few soils were determined in various liquids. (Table 66).

These values are more or less as expected. The difference in the densities of P.C. 13 soil in water and kerosine oil is noticeable. It might be pointed out that P.C. 13 soil contains the highest percentage of the finest particles, which prevent the entry of long-chain molecules or liquids with appreciable contact angles. It is also to be noted that a very small difference in density due to the non-entry of a particular liquid into the finest pores will produce a comparatively larger difference in the heat of wetting, since the highest heat of wetting is produced in the case of the finest capillaries. These results are only qualitative, but they may indicate the cause of the difference between the heat of wetting of water and organic liquids.

TABLE 66. Density of soils in different liquids.

Soil No. P.C.	Alcohol (C_2H_5OH)	Water	Paraffin liquid	Kerosine	Benzene	Toluene	Xylene
13	2.732	2.67	2.34	2.37	2.59	2.595	2.550
123	2.64	2.686	2.61	2.665	2.692	2.685	2.670
111		2.715		2.695			
172	2.62	2.71	2.65	2.52	2.675	2.664	2.661

TABLE 67. Heat of wetting (calories per gram soil) in kerosine after bringing into equilibrium with atmospheres of different humidities.

Soil No.	Relative humidity					
P.C.	0%	10%	30%	50%	70%	90%
13	3.14	2.10	0.92	1.0	−0.115	−0.464
72	0.967	1.06	0.563	0.284	−0.058	−0.28
111	0.966	0.6	0.473	0.137	0	−0.148
123	2.85	1.35	1.030	1.17	−0.057	−0.108
246	2.09	0.823	0.553	0.62	−0.058	0.0
172	2.85	1.32	0.727	0.535	−0.115	0.0
173	2.22	0.703	0.385	0.55	−0.113	−0.30
175	1.23	1.26	0.403	0.34	−0.059	−0.06
Bentonite	5.08	2.50	0.750	0.66	−0.245	−0.058

Heat of Wetting of Soils in Kerosine

If the lower heat of wetting of soils in kerosine, etc., is due to the failure of the long-chain molecules to enter the small capillaries, it follows that if the heat of wetting is measured after allowing the soil to take up moisture from atmospheres of low humidity, when the finer capillaries are closed by the entrance of water, the heat of wetting should be only slightly affected. To test this point, a number of soils were brought to equilibrium with atmospheres of increasing humidities, so that capillaries of different sizes were filled with water, and the heat of wetting was determined in kerosine. (Table 67).

It appears that two factors are involved in these measurements: (1) the mixing of kerosine with water held in the soil and (2) the filling with oil of coarser capillaries unoccupied by water. The first action is probably accompanied by a negative heat effect. This was found actually to be the case by an experiment, in which 5 grams of water, on being mixed with 200 cc of kerosine, gave -3.2 calories. It appears, therefore, that at higher humidities when the quantity of water absorbed by the soil is large, the negative effect predominates; as a result of this the net heat of wetting observed is negative at higher humidities.

Absorption of Water from a Sulphuric Acid-Water Mixture

It has been proved that when a capillary system is brought into equilibrium with an atmosphere of a particular humidity its moisture is under a definite vapor pressure. If this absorbed water is brought into contact with a solution of the same vapor pressure, it is interesting to see whether there is any transference of moisture from the capillaries into the solution. Since any such transference would be indicated in terms of heat, the absence of any rise of temperature would be a strong indication that none has occurred. To study this, experiments were made first with silica samples. About 10 grams of the sample were kept in an atmosphere of 50% humidity, and after it had absorbed the maximum amount of moisture from this atmosphere, its heat of wetting was determined in a sulphuric acid-water misture of a composition corresponding to 50% humidity. It was thought that if no more water were absorbed, the heat of wetting would be practically nil, but the value was found to be 6.45 cal. per gm. of silica; its value in pure water was 9.35.

In another experiment pure, dry silica was taken and its heat of wetting was determined in pure concentrated H_2SO_4. The value was found to be 12.1 cal./gm. of the material as against 23.9 in pure water. This shows that sulphuric acid as such is absorbed in the minute capillaries like any other liquid.

Heat of Wetting of Silicates and Silica in Water at Different Humidities

Silicates of lead, copper, barium, iron and aluminum, as well as mixtures of iron and aluminum silicates of different composition, were prepared by the usual precipitation method. The gels so obtained were washed to remove the salts and then dried. The heat of wetting in water as well as the moisture absorption-vapor pressure curves of these materials were determined.

Portions of these silicates were treated with dilute acid to wash off metallic oxides and the resulting silica was dried in every case after washing with distilled water. The heat of wetting and moisture absorption-vapor pressure curves of the different samples of silica thus obtained were also determined. The results of moisture absorption at different humidities are given in Tables 68 and 69. The

heat of wetting of the silicates as well as of different samples of silica follow the same order as the moisture absorption of these materials (Table 70). Lead and barium silicates absorb comparatively less moisture than other silicates, but the silica obtained from various compounds behave more or less alike.

TABLE 68. Moisture absorption by various silicates at different humidities.

Silicate	% moisture absorbed at different humidities						
	10%	30%	50%	70%	90%	96%	99 5%
Lead	4.42	6.22	6.51	9.05	10.37	12.93	14.22
Copper	7.80	14.34	17.98	26.05	30.17	33.25	34.01
Barium	4.43	6.57	8.10	11.90	15.46	17.80	20.87
Iron	6.51	15.41	18.85	30.70	32.50	34.99	35.56
Aluminum	4.49	11.48	14.36	16.06	20.15	25.51	25.27
75% Fe + 25% Al	6.20	15.0	18.55	29.76	30.56	32.92	33.33
50% Fe + 50% Al	6.51	15.93	18.94	28.41	32.00	34.15	34.25
25% Fe + 75% Al	4.18	12.93	14.97	25.56	28.05	31.21	32.80

TABLE 69. Moisture absorption by silica obtained from various silicates.

Silica from:	% Moisture absorbed at different humidities						
	10%	30%	50%	70%	90%	96%	99.5%
Lead silicate	8.99	16.25	24.97	30.06	39.05	44.9	51.0
Copper "	11.03	17.72	25.54	32.11	39.19	44.73	51.98
Barium "	9.09	16.21	23.28	31.87	40.16	46.73	53.13
Iron "	10.25	16.33	23.88	30.99	37.27	43.01	50.05
Aluminum "	9.88	15.57	23.39	32.00	40.85	44.35	51.09

TABLE 70. Heat of wetting of various silicates.

Silicate	Heat of wetting (cal./gram)	
	Silicates	Silica obtained from silicates
Lead	8.44	23.9
Copper	15.3	24.64
Barium	11.2	22.16
Iron	15.8	25.19
Aluminum	15.4	22.20
75% Fe + 25% Al	15.3	24.56
50% Fe + 50% Al	16.5	20.16
25% Fe + 75% Al	14.2	24.16

From these results the heat of wetting per gram of water absorbed by 100 grams of materials at different humidities was calculated for mixtures of iron and aluminum silicates only, just as in case of soils (Table 62). The values are given in Table 71. It is interesting to note that the averages in case of soils and silicates, though not quite identical, follow the same order.

The heats of wetting of the various silicates, as well as of silica before and after activation, were calculated from their moisture-absorption values, and average values of heat of wetting at different humidity intervals are given in Table 71. These calculated

TABLE 71. Heat of wetting for 1 gram of water absorbed at different humidity intervals by 100 g of material.

Mix No.	Composition		Heat of wetting (calories) at various humidities					
	Iron silicate	Aluminum silicate	0-10%	10-30%	30-50%	50-70%	70-90%	90-100%
1	100%	0%	1.41	0.87	1.16	0.20	0.38	0.27
2	75%	25%	1.16	0.90	1.03	0.20	0.50	0.27
3	50%	50%	0.7	0.88	1.74	0.11	0.33	0.35
4	25%	75%	2.4	0.91	0.90	0.24	0.34	0.21
5	0%	100%	1.6	1.06	1.30	1.5	0.18	0.10
Average			1.45	0.92	1.22	0.18	0.34	0.24
Average obtained in soils			1.78	0.47	0.73	0.5	0.18	0.10

TABLE 72. Comparison of calculated and determined values on heat of wetting of silica and silicates.

Mix No.	Composition		Heat of wetting (calories/gram of material)		
				Calculated	
	Iron	Aluminum	det'd	from silicate average	from soil average
1	100%	0%	25.0	25.31	24.82
2	75%	25%	22.5	24.42	23.78
3	50%	50%	21.0	25.20	24.80
4	25%	75%	24.3	20.45	19.26
5	0%	100%	22.6	20.38	16.40
6	Silica (unactivated)		10.5	9.17	9.96
7	Silica (activated)		18.6	17.75	17.76
8	Lead silicate		8.44	10.26	10.81
9	Copper silicate		15.3	25.58	24.80
10	Barium silicate		11.2	13.43	12.93

values of heat of wetting are to be compared with the determined values in Table 72.

It will be seen that results with ferroaluminosilicates are similar to those of soils. Using the mean value for heat of wetting of soils for various humidity intervals (Table 62) or similar values for silicates (Table 71), we can calculate the heat of wetting of the various silicates.

Effects of Various Treatments on Heat of Wetting of Soils

It is evident from the results mentioned in the foregoing that since the heat of wetting of soil is due to the absorption of the liquid in the micropores of the particles, any treatment that would affect moisture absorption would cause a corresponding change in

the heat of wetting. To adduce evidence on this point, a few soils were subjected to some treatments which were considered likely to affect their hygroscopicity and the heat of wetting was determined before and after. The treatments given were (1) heating to various temperatures, (2) leaching with acid solution of different strengths, and (3) activation at 200°C in a current of CO_2 for two hours.

Heating to various temperatures. It has been shown that soils undergo progressive decrease in hygroscopicity on heating, to increasing temperatures.

TABLE 73. Effect of heating soils at different temperatures on their heat of wetting.

Soil No.	Heat of wetting (calories per gram of soil)				
P.C.	100°C	200°C	300°C	400°C	500°C
13	10.9	13.72	8.99	6.08	5.91
72	4.75	3.99	3.8		3.2
123	5.48	5.38	5.38	6.08	5.82
111	1.42	1.01	0.90	0.51	
172	7.625	7.77	6.75	0.81	

The heat of wetting would therefore be expected to show a corresponding decrease. Five soils were selected for this purpose and were heated for 6 hours at different temperatures before determining their heat of wetting. The results are given in Table 73. It will be seen that P.C. 13 shows a slight increase in the value when heated at 200°C, followed by a progressive decrease when heated to increasing temperatures. The increase up to 200°C in this soil is due to the fact that some of the residual moisture which cannot be easily removed at 100-110°C is driven out on heating to 200°C, and the soil is dry in the true sense at this temperature only. Heating to higher temperature leads to the progressive "fusion" of ultra-clay and consequent decrease in the volume of the capillaries. As a result of this the hygroscopicity is appreciably decreased and the heat of wetting shows a corresponding decrease. Other soils behave similarly, except P.C.123, which gives an almost constant value for heat of wetting at all temperatures. This is probably because in this soil, on account of its refractory nature, the fusion of clay and ultra-clay particles does not take place till a much higher temperature is reached.

Leaching with acid solutions of different strengths. It is well known that, on treatment with acids of moderate strength, soils undergo partial decomposition, a part of the sesquioxides being washed out. This should result in partial breakdown of the soil structure due to dissolution of some ultra-clay particles which are associated with some of the finest capillary spaces so closely involved in the moisture-absorption capacity of soils. It would be expected, therefore, that treatment of soil with acid solution of increasing

strengths should lead to progressive decrease in its heat of wetting. To test this, a sample of bentonite was selected, as this is rich in ultra-clay and therefore particularly suitable for this purpose. 25-gram portions of the sample were leached separately over a Buchner funnel with 2 liters of N, 2N and 4N HCl solutions, followed by leaching with water to remove chloride ions. The results of the heat of wetting determinations are given in Table 74. It is evident that on account of the dissolution of the finer particles there is a corresponding decrease in the heat of wetting.

Activation in a current of CO_2 at 200°C for two hours. As water held up by soils in the small capillaries has different values of vapor pressures, depending upon the size of capillary spaces, some of it in the minutest capillaries, on account of its relatively lower vapor pressure, cannot be driven out completely on heating

TABLE 74. Effect of acid treatment on the heat of wetting of bentonite.

Heat of wetting (calories per gram)			
Before treatment	Leached with normal HCl	2 liters of 2N HCl	2 liters of 4N HCl
22.54	16.60	14.1	12.1

TABLE 75. Effect of activation on heat of wetting of soils.

Soil No. P.C.	Heat of wetting (calories per gram soil)	
	Before activation	After activation
6	2.336	3.93
13	10.9	14.74
123	5.48	5.46
172	7.62	9.9

to 110°C or even higher. This is true of all capillary systems, including silica, alumina, etc. To remove the last traces of water, these porous substances are usually activated in a current of dry air or some gas at 200°C for a couple of hours. It was thought of interest to activate a few soils in this manner and to compare their heat of wetting before and after activation (Table 75). It will be seen that activation, as expected, leads to increased value for heat of wetting, except in the case of P.C. 123, which is singularly deficient in ultra-clay.

Effect of Exchangeable Bases on Heat of Wetting

Heat of wetting with single-base soils was studied by Pate, who concluded that soil with a monovalent base gives a lower heat of wetting than soil with a divalent base. These conclusions were confirmed by the author. The heat of wetting of single-base soils in equilibrium with different humidities has not been measured heretofore.

Single-base soils were prepared from soil P.C. 13 by 0.05N HCl treatment, followed by neutralization with various hydroxides. The

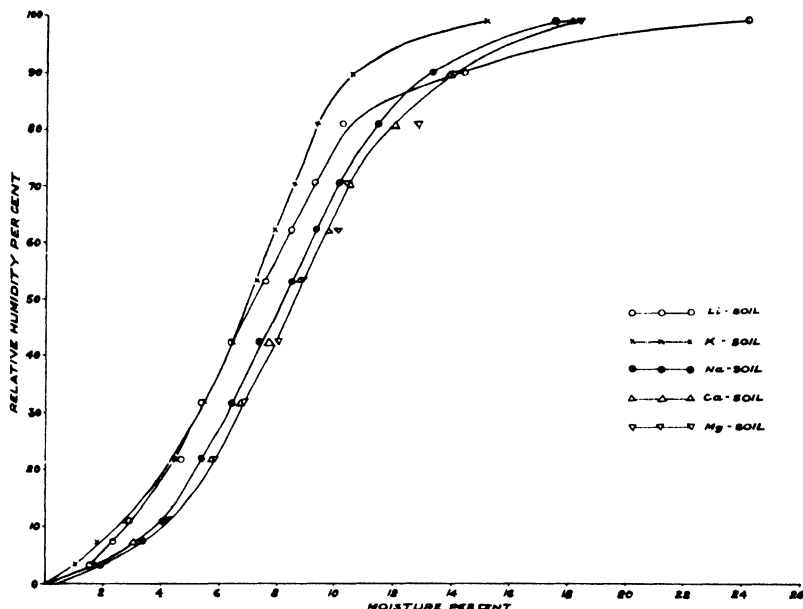



Fig. 48. Relation Between Relative Humidity and Moisture Content of Soils Containing Different Single Bases

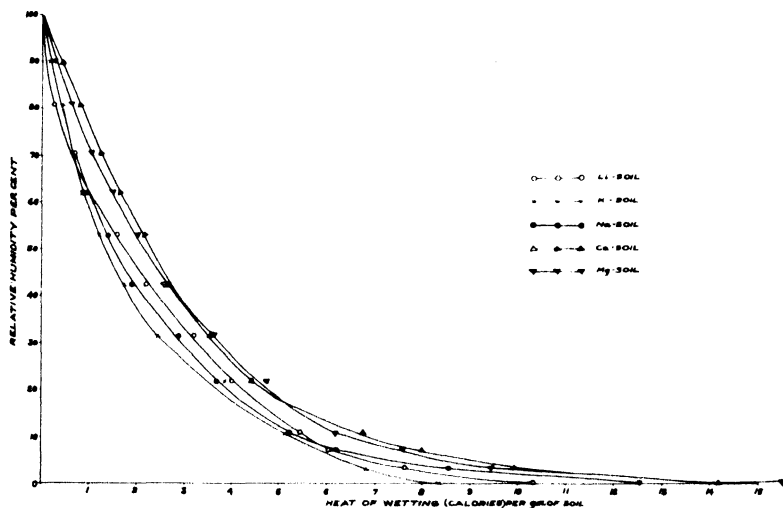



Fig. 49. Relation Between Relative Humidity and Heat of Wetting of Soils Containing Different Single Bases

moisture-humidity curves of the soils are given in Fig. 48, and the heat of wetting curves in Fig. 49. The lower heat of soils with monovalent exchangeable bases, as compared with divalent, is rath-

er extraordinary. In view of the high hydration of Li and Na soils, one would have expected that the heat of hydration would be added to the heat of wetting, and that a higher value would result. A possible explanation of this difference might lie in the fact that monovalent bases are ionized to a greater extent on the soil surface and the negative heat of ionization might lower the heat of wetting correspondingly.

If the micropore hypothesis - which offers a purely physical explanation of the mechanism of moisture absorption - is correct, we should expect all other liquids that can wet the soil, and consequently enter into the micropores, to show a heat of wetting not far from that with water. On the other hand, if the micropores are partly filled with water, the heat of wetting of the moist soil with organic liquids can be modified in two ways, as follows:

The heat of dilution of the water contained in the soil, with that of the organic liquid, if positive, will be added to, and if negative will be subtracted from, the heat of wetting of the moist soil.

The radius of curvature of the capillary water will be affected by the change in the surface tension of water in air, being replaced by the interfacial tension of the organic liquid and water. In other words, a liquid with a low interfacial tension would reduce the radius of curvature and cause the moist soil to appear wetter at a particular humidity, and thus lower the heat of wetting correspondingly.

We can test both these possibilities by determining the heat of wetting of soils in equilibrium with different humidities, using organic liquids of known interfacial tension and heat of dilution with water. The following liquids were chosen:

	Surface tension (dynes)	Interfacial tension (dynes)
Benzene	28.86	35.00
Aniline	42.58	5.77
Carbon tetrachloride	26.66	45.0

The heat of wetting of soil P.C. 13 kept at various humidities and consequently containing different amounts of moisture was studied. The curves showing the relation between heat of wetting and the relative humidity with which the soil was in equilibrium are shown in Figure 50. It will be seen that the heat of wetting is lowered at all humidities in the case of organic liquids. From the lowering of the freezing point of benzene by moist soils in equilibrium with different humidities, it was concluded that the abnormal behavior of soils as compared to H_2SO_4 - water mixtures and other hygroscopic substances is due to the fact that water-benzene interfacial tension is lower than water-air surface tension and that, therefore,

a corresponding change in the radius of curvature of the water held in the minute capillaries is possible. It was shown that

$$p''/p' = (p'/p)\ 0.478$$

where p is the vapor pressure at a plane surface, p' the vapor pres-

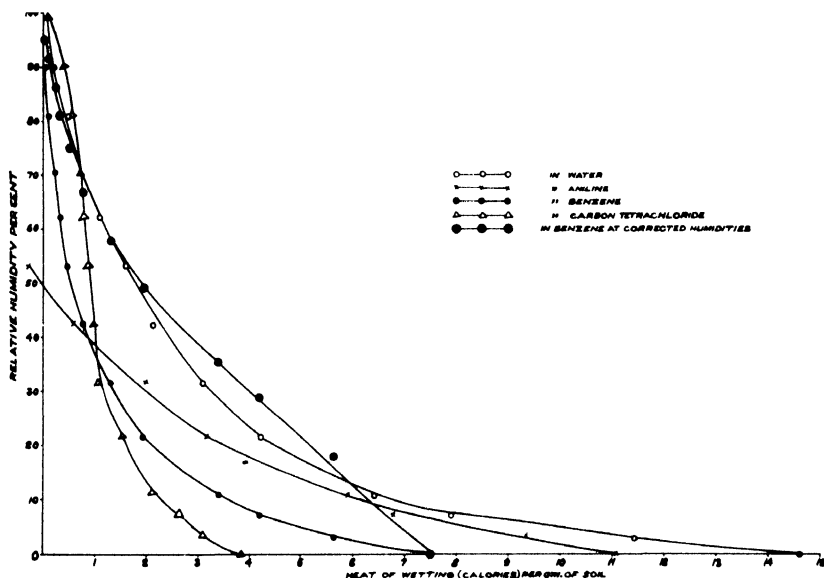



Fig. 50. Heat of Wetting of Soil in Different Liquids

sure at the curved surface, and p'' the aqueous vapor pressure at a water-benzene surface for the same capillary (Chapter VI).

Thus the soil in equilibrium with a particular humidity appeared wetter when brought into contact with benzene, as if it were in equilibrium with a higher humidity. This conclusion seemed to conform to the data on the heat of wetting with benzene; consequently if we calculate the relative humidity of the soil in contact with benzene by the formula given above, and interpolate the heat of wetting corresponding to the corrected value from the curve, the corrected values fall on the heat of wetting curve for water. These values are shown in Fig. 50. If, however, we calculate similar values for aniline or carbon tetrachloride by substituting the interfacial tensions of these compounds, we get a very poor fit. Very likely this may be due to the poor wetting power or the high value of the contact angle of these liquids for soil.

CHAPTER XII

ABSORPTION OF MOISTURE AND ORGANIC VAPORS BY SALT HYDRATES

Among substances that can absorb water from the vapor phase, hydrates occupy a unique position. Unlike capillary systems in which absorption takes place at all humidities, hydrates have a critical vapor pressure, below which no absorption is possible. Hydrates, therefore, would correspond to a capillary system in which all the micropores are of the same diameter, so that moisture is unable to condense in them unless the relative humidity is greater than the vapor pressure of the water condensed in the capillaries. The fact that the entire moisture is lost or gained within a narrow range of humidity can only be reconciled with the view that the capillaries in this case do not possess a cellular structure, but are cylindrical (without any corners), so that all the water can evaporate without altering the radius of curvature of the absorbed water. With salts that form more than one hydrate, more than one size of micropores would be postulated in the space lattice, requiring a definite number of water molecules to fill them completely. This micropore theory of salt hydrates may at the first sight appear in conflict with the chemical view so far presented. It may also appear unnecessary in view of the well-established stoichiometric relationship. The fact that salt hydrates exist even in solution would also seem contrary to the existence of micropores.

A simple chemical concept based on residual valencies would no doubt be adequate to explain all the phenomena associated with salt hydrates. For the present, however, our object is merely to establish an analogy, to prove that chemical forces associated with residual valencies may have something very much in common with surface tension effects in micropores. The two may originate from the same source. The surface tension of liquids is very likely a manifestation of the residual valencies - the unsatisfied lines of force, the seat of potential energy.

It has always been a puzzle why water rises in a capillary tube. What is the hook that pulls it up? What is the reality behind the phenomenon of surface tension? Is it confined only to the monomolecular surface layer or does it extend deeper into the body of

the liquid, with gradually decreasing intensity? Atoms and molecules in the gaseous state have four-dimensional freedom; in monomolecular films they have two-dimensional freedom; in solids and liquids in bulk they have freedom in one direction only. It is this freedom that constitutes free energy, or surface tension, or residual valency. The analogy between the formation of salt hydrates and the filling of micropores, therefore, may not be altogether superficial.

We have to consider in the first instance whether anhydrous salts have micropores. It would appear to be a logical consequence that when water evaporates from a hydrate, it must leave gaps corresponding to the water that has evaporated. On the other hand, since a crystalling hydrate falls to an amorphous powder, it may be supposed that the space lattice has collapsed and individual molecular groups have fallen apart. The mechanism of moisture absorption would be different in the two cases. If micropores exist, the moisture absorption would be due to capillary condensation; otherwise water molecules would simply attach themselves to molecular groups by residual chemical valencies. In the former case liquids other than water could also condense in the micropores, whereas in the latter no such condensation would be possible.

It is conceivable that residual valencies that can attract and bind water could operate in the case of organic liquids that may have no chemical affinity for the anhydrous salt. On the other hand, if micropores are present, then almost any liquid might be absorbed, the only limiting factor being the contact angle. The existence of micropores could also be demonstrated by measuring the heat of wetting of the anhydrous salt with organic liquids and with water.

The existence of hysteresis effect in the hydration and dehydration of salt hydrates would constitute another argument in favor of the micropore theory, for it is inconceivable that a purely chemical reaction should not be strictly reversible as regards the vapor pressure at which the hydrate is completely transformed into the anhydrous state, or vice versa.

Precision will be gained if we treat the absorption of water by salt hydrates in exactly the same manner as we have been treating capillary absorbents. Anhydrous salts, therefore, were allowed to absorb moisture in atmospheres of varying relative humidity in desiccators containing appropriate mixtures of sulphuric acid and water. The various hydrates are dealt with under their appropriate headings.

Sodium Sulphate

The amounts of moisture absorbed from atmospheres of different humidities by anhydrous sodium sulphate are given in Table 76. The relative vapor pressure of the system $Na_2SO_4 . 10H_2O$ - Na_2SO_4 at 15°C is 72.5%. The vapor pressure of this system, therefore, must exceed this limit before water can be absorbed by the anhydrous

salt. When the maximum amount of water corresponding to $Na_2SO_4 \cdot 10H_2O$, *i.e.*, 126% has been taken up, no more moisture from any higher humidity is absorbed. This moisture it can take up from any humidity higher than 72.5%, provided sufficient time is allowed for the state of equilibrium. It is to be noted that the rate of absorption of moisture is extremely slow in the case of hydrates. Equilibrium has not been attained even in 54 days at 76.4% and 82.2% humidity. This is unlike the behavior of capillary systems in which the rate of moisture absorption is fairly rapid as a rule.

TABLE 76. Absorption of moisture by anhydrous sodium sulphate.

Days	% Moisture absorption at different humidities							
	10%	33%	50%	70%	76.4%	82%	90%	99%
6	0.096	0.18	0.18	0.72			23.5	20.5
7	0.096	0.18	0.18	0.72	21.5	18.9	30.5	26.9
17	0.50	0.52	0.44	0.82	48.3	41.8	92.0	91.7
47	0.51	0.52	0.56	0.82	95.0	92.8	127.3	123
54	0.60	0.62	0.64	0.85	102.3	101.9	129.6	127

Hysteresis in moisture absorption of sodium sulphate. The wetting and drying data at different humidities are given below:

Humidity (%)	10	33	50	70	82.2	90
Moisture (%) wetting	0.60	0.62	0.64	0.85	101.9	129.5
Moisture (%) drying	0	0	0	0.42	102.5	123.6

The above results indicate almost complete absence of hysteresis, hydration and dehydration taking place at the same critical vapor pressures. The results, however, are misleading in two respects. In the first instance if the critical vapor pressure of $Na_2SO_4 - 10H_2O$ is 72.5%, why should any drying take place at 82.2% humidity unless it corresponds to $Na_2SO_4 - 8H_2O$, which in all probability must occur at a lower humidity than 72.5%?

There is practically no absorption of organic vapors by sodium sulphate when it is dehydrated at high temperature. There is, however, some indication of organic vapor absorption by sodium sulphate when it is dehydrated over H_2SO_4 at low temperature.

Copper Sulphate

The results of moisture absorption by anhydrous copper sulphate are given in Table 77, and plotted in Fig. 51. The maximum amount of moisture taken up is approximately 56%, which is equal to the amount required to form $CuSO_4 \cdot 5H_2O$. Further, this amount is taken up from 50% humidity, which is in accord with the vapor pres-

TABLE 77. Moisture content of copper sulphate in equilibrium with different humidities.

Relative humidity (%)	Equilibrium moisture content (%)			
	Wetting	Drying Values		
		7 days	29 days	37 days
0	0.07	0.19	0.11	0.11
2.25	0.16	1.8	1.21	1.19
5.1	1.35	2.4	2.32	2.21
7.6	1.98	2.22	2.16	2.16
10.4	2.20	7.3	6.97	6.97
15.8	7.28	8.7	6.98	6.98
20.4	8.60	9.7	9.2	9.16
25.2	9.68	13.5	13.14	13.02
30.0	13.70	23.8	19.76	18.45
41.4	23.60	52.7	43.78	42.21
50.7	52.9	53.4	52.97	52.87
61.0	54.4	54.6	54.59	54.61
71.8	53.44	53.6	53.72	53.72
82.2	55.02	53.5	53.61	53.61
90.7	52.62	53.9	53.98	53.87
96.0	53.80	54.2	53.97	53.97
98.7	55.91			

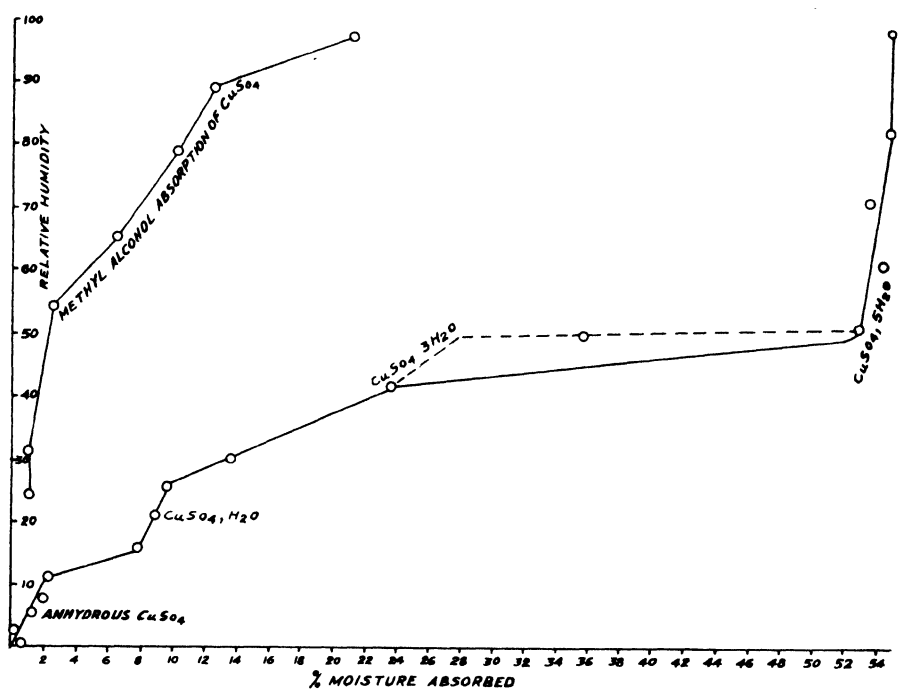



Fig. 51. Vapor Pressure Curves of $CuSO_4$ with Water and Methyl Alcohol

sure of the system $CuSO_4 . 3H_2O - 2H_2O - CuSO_4 . 5H_2O$. A close perusal of the results in Table 77 and Fig. 51 reveals certain peculiarities which require mention. There are definite breaks in the vapor pressure-moisture content curve, but the exact points of inflection corresponding to the different hydrates are approached much more gradually than has hitherto been supposed. The whole curve approximates more closely a capillary-cumchemical absorption. It is significant, however, that practically all the points can be fitted on the dotted line curve which approximates the usual type of hydrate vapor-pressure curve.

In the case of $CuSO_4$, equilibrium is reached much more quickly than in the case of Na_2SO_4. The values recorded in Table 77 were obtained after 37 days' exposure, though equilibrium was attained in about 15 days.

TABLE 78. Absorption of organic liquids by $CuSO_4$ from atmospheres of different relative vapor pressures (R.V.P.).

R.V.P.	CH_3OH absorbed (%)	R.V.P.	Acetone absorbed (%)	R.V.P.	Benzene absorbed (%)
24.1	1.14	14.5	7.09	91.26	4.6
31.1	1.06	47.8	7.50	100	3.9
54.22	2.43	67.5	7.50		
65.3	6.51	100	6.91		
77.10	10.32				
88.74	12.58				
95.1	21.82				

Absorption of Organic Vapors. The absorption of methyl alcohol, acetone and benzene was studied from atmospheres of different relative vapor pressures, which were obtained by mixing glycerol with methyl alcohol, oleic acid with acetone, and naphthalene with benzene (Table 78). The results of methyl alcohol absorption are also plotted in Fig. 51, together with those of water. A close similarity between the two curves is apparent. These results can best be interpreted on the basis of capillary condensation, followed by a dissolution of the walls of the capillaries in the case of water. The constant value for acetone and benzene can be reconciled with the view that only capillaries of a certain dimension are accessible to these liquids. This is not surprising when it is remembered that the accessibility of a liquid to a micro-capillary depends on the contact angle, which again depends not only on the nature of the liquid but on the size of the capillaries.

Calcium Sulphate

Results of moisture absorption at various humidities are given in Table 79. $Ca SO_4 . 2H_2O$ was dehydrated at different temperatures and moisture absorption studied with each. The results show that the hemi-hydrate is first formed at about 10% humidity (the

theoretical amount of moisture is about 26%). It is interesting to note that if gypsum is dehydrated above 200°C, the resulting anhydrous salt loses its capacity to form hydrates at all. To find the exact temperature at which this property is lost, gypsum was heated at various temperatures in a paraffin bath with exact temperature control (Table 80 and Fig. 52). It is clear that there is a gradual decrease in moisture absorption between 180 and 188°C.

TABLE 79. Moisture absorption-vapor pressure relationship of anhydrous $CaSO_4$.

Relative humidity (%)	% Moisture after exposure for 7 and 14 days					
	Heated to 170°C		Heated to 200°C		Heated to 1200°C	
	7 days	14 days	7 days	14 days	7 days	14 days
10.4	4.77	5.26	0.76	0.96	0.71	0.71
30.0	3.49	4.88	0.65	0.97	0.71	0.71
50.7	6.00	6.60	0.68	0.50	0.40	0.40
70.0	5.57	5.88	1.60	1.78	0.91	0.85
90.0	6.65	6.85	1.30	1.49	0.87	0.87
98.7	17.90	22.80	4.68	5.10	3.87	3.69

TABLE 80. Effect of temperature of dehydration on moisture absorption by $CaSO_4$.

Temperature (°C)	Moisture absorbed at 98.7% humidity	
	4 days (%)	7 days (%)
172	19.50	20.16
175	16.40	18.95
180	18.32	20.05
181	18.06	18.98
182	14.39	15.135
183	14.03	14.97
184	12.10	12.76
185	12.23	12.75
186	13.16	13.29
187	6.95	6.87
188	3.75	3.71
189	3.95	3.95
192	4.62	4.96
195	2.91	3.02
198	3.67	3.87

Another interesting property of $CaSO_4 . 2H_2O$ is that it cannot be dehydrated by drying at ordinary temperature alone. This will be clear from Table 81, in which the equilibrium moisture contents of hydrated $CaSO_4$ dried at various humidities are given. These results should be compared with those in Table 79, in which it is shown that anhydrous $CaSO_4$ takes up only 6.85% moisture from an atmosphere of 90% humidity.

Absorption of organic vapors. There is very little absorption of organic vapors by dehydrated $CaSO_4$; the results, however, are parallel to those of moisture absorption, as will be clear from Table 82.

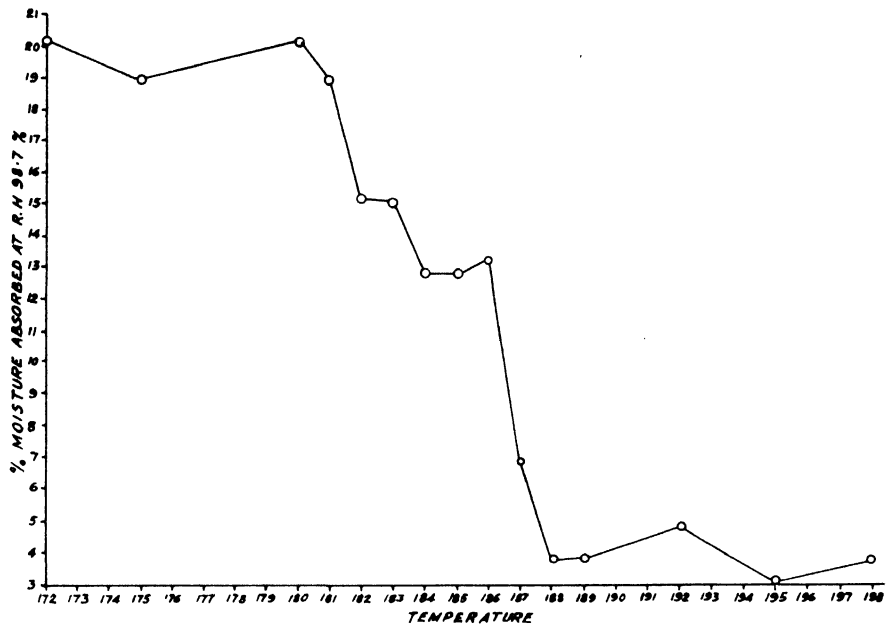



Fig. 52. Effect of Temperature of Dehydration on Moisture Absorption by $CaSO_4$

TABLE 81. Drying of $CaSO_4 . 2H_2O$ at different humidities.

Relative humidity (%)	Moisture content when dried for		
	8 days (%)	17 days (%)	31 days (%)
10.4	15.02	15.13	14.92
30.0	15.41	15.31	14.81
50.7	20.95	17.56	16.61
70.0	21.64	20.90	18.82
90.0	22.73	21.97	20.56

TABLE 82. Absorption of organic vapors by $CaSO_4$ from atmospheres of different relative vapor pressures (R.V.P.).

R.V.P. (%)	CH_3OH absorption (%)	R.V.P. (%)	Acetone absorption (%)	R.V.P. (%)	Benzene absorption (%)
24.1	1.23	14.5	0.31	91.26	2.58
31.1	1.01	47.8	0.48	100	2.51
54.2	1.34	67.5	1.20		
65.3	1.20	100	4.70		
77.1	1.20				
86.7	1.61				
95.1	3.10				

Potash Alum

Alums are unique among hydrates insofar as they are associated with as many as 24 molecules of water. Potash alum was dehydrated at 200°C. Another portion was heated directly over a Bunsen flame to determine the effect of high temperature on its moisture-absorption capacity, as in the case of $CaSO_4$ (Table 83).

It will be seen that the temperature of dehydration has a pronounced effect on moisture absorption, though not so much as in the case of $CaSO_4$. The dehydration of alum, like $CaSO_4$ cannot be carried out at the ordinary temperature by lowering the humidity. The theoretical amount of moisture required to form hydrated alum is about 84%, and most of it is taken up at 70% or higher humidity.

TABLE 83. Moisture content of potash alum kept at various humidities.

Humidity	Moisture percentage					
	10%	30%	50%	70%	90%	99%
(A) Dehydrated at 200°C						
(a) Wetting values after 10 days	1.05	1.7	4.74	74.45	78.43	82.65
(b) Drying values after						
8 days	79.91	80.1	79.9	80.07	81.2	
19 days	79.91	80.1	79.76	80.0	81.2	
31 days	79.87	80.1	79.53	79.49	80.96	
(B) Dehydrated over Bunsen flame						
(a) Wetting values after 10 days	0.1	0.16	0.74	21.38	72.08	77.9
(b) Drying values after						
8 days	52.9		58.03	59.8	77.30	
19 days	52.79		58.0	59.93	77.12	
31 days	51.16		58.0	58.81	76.32	

The dehydration, however, cannot be carried out even in an atmosphere of 10% humidity. There is practically no absorption of organic vapors by potash alum when it is dehydrated at high temperature. There is some indication of organic vapor absorption by alum when it is dehydrated over H_2SO_4 at low temperature.

Zinc Sulphate

The salt was dehydrated by heating to 450°C, at which temperature it is known to lose all its water of hydration. The wetting and drying values are given in Table 84. It will be seen that within 10% humidity $ZnSO_4 . H_2O$ is formed (theoretical amount is about 11%). At about 70% humidity $ZnSO_4 . 6H_2O$ is formed (theoretical amount is about 67%); or probably $ZnSO_4 . 7H_2O$ for which the theoretical amount is 78%. Water, however, continues to be taken even beyond

this value at higher humidities, a phenomenon characteristic of deliquescent salts. It is significant that though the deca-hydrate is formed at 70% humidity on wetting, drying at 50% humidity does not result in the formation of the mono-hydrate, which occurs at 30% humidity.

Calcium Chloride

Fused calcium chloride was taken. The drying and wetting values are given in Table 85. The wetting values show that the di-hydrate is produced within 10% humidity and the hexa-hydrate is formed even below 30% humidity. At higher humidities water is taken up on account of the deliquescent nature of the salt.

TABLE 84. Wetting and drying values of moisture content of zinc sulphate.

Humidity	Moisture percentage					
	10%	30%	50%	70%	90%	99%
Wetting values after 10 days	10.73	12.5	13.17	64.5	116.6	192.1
Drying values after 8 days	17.4	60.25	61.2	77.67	173.5	
17 days	12.4	14.52	66.2	72.4	138.5	

TABLE 85. Wetting and drying values of moisture content of calcium chloride.

Humidity	Moisture percentage					
	10%	30%	50%	70%	90%	99%
Wetting values after 10 days	39.06	117.2	191.59	255.9	231.9	479.13
Drying values after 8 days	70.11	130.1	194.8	290.4	455.04	
31 days	62.6	117.45	169.5	230.9	413.5	

The absorption of organic vapors, as in the case of other hydrates, shows a striking parallelism with the absorption of water vapors. With methyl alcohol even the phenomenon of deliquescence is shown, as is clear from the results given in Table 86.

Heat of hydration. The heat of hydration of salt hydrates is analogous to the heat of wetting well known in capillary systems. A known weight of the anhydrous salt was added to a known weight of the saturated solution of the salt held in a Dewar flask and the rise of temperature noted; from this the heat of hydration was calculated. It was assumed that since water was already saturated with the salt there was no heat of solution. In Table 87 are given values for heat of hydration for the various hydrates in calories per gram of water

taken up by 100 grams of the salt. This value was obtained by dividing the total heat of hydration per 100 grams of the salt by the amount of moisture absorbed. This method of representation was preferred for ease of comparison with similar results obtained with soils. Such results with soils are included in the table. It will be seen that the order of heat of hydration is the same as that of the heat of wetting of soils. The heat of wetting for organic liquids for both soils and hydrates is also of the same order.

TABLE 86. Absorption of organic vapors by anhydrous $CaCl_2$ from atmospheres of different relative vapor pressures (R.V.P.)

R.V.P. (%)	CH_3OH absorbed (%)	R.V.P. (%)	Acetone absorbed (%)	R.V.P. (%)	Benzene absorbed (%)
24.1	55.2	14.5	72.4	91.26	28.25
31.1	54.6	47.8	72.1	100	27.59
54.2	122.4	67.5	112.2		
65.3	155.8	100	112.8		
77.1	216.5				
86.74	353.6				
95.1	518.0				

TABLE 87. Heat of hydration of salts and heat of wetting of soils per gm. of liquid absorbed by 10 g of salt or soil.

Substance	Water	CH_3OH	$C2H_5OH$	Acetone	Benzene
Soil P.C. 13	1.13	0.74	0.82	0.88	0.66
Soil P.C. 72	0.73	0.608	0.54	0.93	0.5
Soil P.C. 111	0.616	1.4	0.49	2.0	1.3
Soil P.C. 123	0.38	0.38	0.47	0.81	0.39
Soil P.C. 246	0.84	0.99	0.88	0.96	0.44
Soil P.C. 172	0.968	2.6	0.82	1.15	1.1
Soil P.C. 173	0.79	0.967	0.78	1.45	1.58
Soil P.C. 175	0.752	0.42	0.72	0.80	1.60
$CuSO_4$ anhydrous	0.908	0.74	0.85	1.28	0.23
$ZnSO_4$ "	0.76	0.52	0.83	1.17	0.54
$CaSO_4$ "	0.71	0.8	0.403	0.99	0.09
Na_2SO_4 "	0.538	1.0	1.56	0.95	2.4
Potash Alum "	0.66	0.68	0.34	1.08	0.09

The heat of wetting of soils at different humidities can also be compared to the heat of hydration of salts at different vapor pressures. It has been shown in the case of capillary systems that heat of wetting per gram of water absorbed decreases as the relative humidity increases. This is explained by the theory that, since smaller capillaries are involved in the absorption of vapor at lower humidities, the compression on the absorbed water, as well as the heat of wetting, is greater than at higher humidities. The heat of wetting was determined in the case of a soil (P.C.13) and anhydrous $CuSO_4$ after bringing them into equilibrium with atmospheres of

varying humidities (Fig. 53). The striking similarity of the two curves is apparent. The stepwise decrease of heat of wetting for $CuSO_4$ is in line with the fact that the capillaries in the case of salt hydrates are not of continual varying size as in the case of capillary systems.

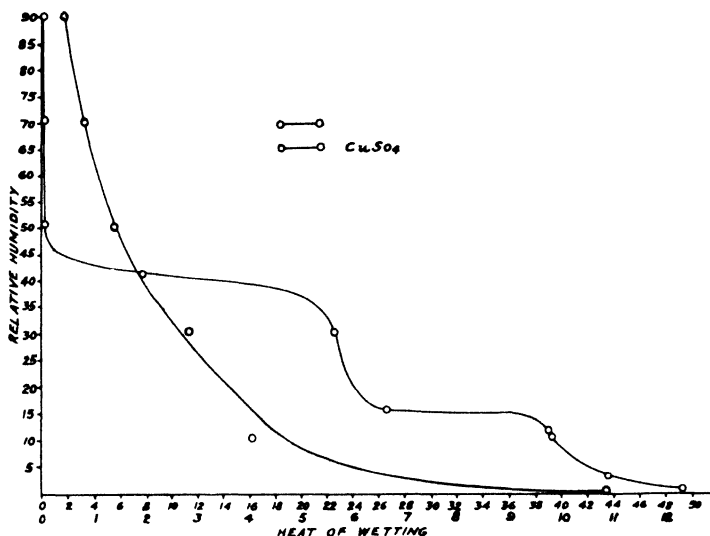



Fig. 53. Heat of Wetting of Soil P.C. 13 and $CuSO_4$ at Various Humidities

Since there is a definite transition temperature above which Na_2SO_4 is supposed to exist as an anhydrous salt, we can study the cooling curve of this salt to throw light on the mechanism of hydrate formation. It is obvious that if a hydrate of Na_2SO_4 is formed at 32°C, there could be a sudden rise of temperature at this point, when a solution of $NaSO_4$ is allowed to cool. The cooling curve, however, showed no such rise of temperature (Fig. 54), in a solution of this salt.

If heat of wetting of anhydrous $NaSO_4$ is due to the formation of the hydrate, which takes place only below 32°C, then there should be no heat of hydration above this temperature. The heat of wetting of anhydrous $NaSO_4$ was determined in a saturated solution of the salt at various temperatures. The results, given in Table 88, show that beyond a gradual decrease of heat of hydration there is no sudden drop at the transition temperature. Similar results with soil P.C.13 are also included in this table. It is seen that there is a much greater decrease in the heat of wetting of soil when the temperature is raised. However, the analogy between heat of hydration and heat of wetting is quite apparent.

Discussion of Results

A number of hydrates have been examined, and the results of moisture and organic vapor absorption can best be interpreted on

the basis of capillary condensation in the micropores, followed by solution of the salt in the capillary-condensed water. The size, the shape, and the space configuration of the capillaries determine the crystal structure, the vapor pressure and the ease of absorption of

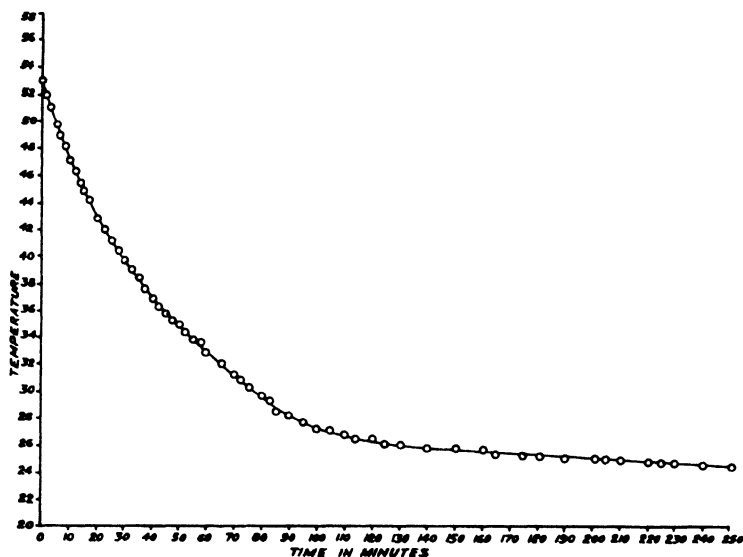



Fig. 54. Cooling Curve of Sodium Sulphate Solution

TABLE 88. Heat of wetting of Na_2SO_4 and Soil P.C. 13 at different temperatures.

Temperature (°C)	Heat of wetting (calories per 100 g of substance)	
	Na_2SO_4	Soil P.C. 13
16	41.20	11.02
22		9.68
25	41.34	
35		9.23
40	35.36	
50		4.31
60	33.29	6.0
80	35.76	5.34
87	29.75	
90		1.39
92		

vapors. The distribution of moisture in a capillary structure depends on the size distribution of particles and the geometry of the pore space. In the case of salt hydrates this distribution depends on the geometry of the space lattice. The fact that a definite number of water molecules are involved in the formation of salt hydrates is purely incidental, and is no proof of the chemical combination of the two molecular species. Intramolecular forces must tend to the formation of geometrical patterns with pore spaces of fixed dimensions, in which a definite number of molecules of water can

be accommodated. It is not unlikely that the walls of the micro-capillaries in salt hydrates are of molecular dimensions and may collapse to some extent on dehydration. If the geometry of the pore space of capillary systems could be described as cellular, the pores in salt hydrates would be appropriately visualized as honeycombed. With this structural difference the entire behavior of salt hydrates may be reconciled with that of capillary systems.

The presence of hysteresis effect, the magnitude of the heat of hydration, which is comparable to heat of wetting of capillary systems, and the general trend of the vapor-pressure curve all point to the general similarity of forces involved in moisture absorption by dehydrated salts as well as in capillary systems.

Absorption of organic vapors by dehydrated salts can be accounted for only by the capillary hypothesis. The fact that dehydrated salts like Na_2SO_4 and potash alum are not wetted by organic liquids and, therefore, are not absorbed clinches the argument in favor of this hypothesis.

Hydrates are supposed to exist in solution and to possess well-defined transition temperatures. It is, however, not clear whether or not hydration and dehydration in solution is accompanied by any thermal change. Theoretically the heat of hydration should be the same, whether it takes place in solution or with a solid anhydrous salt. It is found, however, that there is no thermal change when hydration is allowed to take place in solution. It is only when solid anhydrous salt is brought into contact with water that heat of hydration manifests itself. Here it is much more likely that this is due to the absorption of water or salt solution in the minute capillaries of the anhydrous salt.

The object of introducing the whole discussion about salt hydrates is merely to point out a certain analogy between capillary moisture and water of hydration. It should be pointed out that the analogy breaks down when the influence of organic liquids on the vapor pressure of salt hydrates is considered. In this case, unlike the capillary moisture, there is no change in the surface tension of water of hydration. Hysteresis effect is also partly superficial, because since the crystal structure breaks down on dehydration it is not certain how far the decrease in moisture absorption is due to this cause alone. Absorption of gases and adsorption of solute from immiscible organic liquids, characteristic of capillary moisture, is also not shown by water of hydration.

All this leaves us in a state of uncertainty as to how far the forces involved in the absorption of capillary moisture are chemical and what part is played by purely surface tension effects. However, since surface tension itself may be due to molecular orientation, and residual chemical valencies, a certain amount of analogy between the behavior of water of hydration and capillary moisture is only to be expected. Differences, on the other hand are so striking that substances possessing a capillary structure undoubtedly form a class by themselves.

CHAPTER XIII

DISTRIBUTION OF SOLUTE BETWEEN CAPILLARY WATER AND SOME IMMISCIBLE LIQUIDS, AND SOLUBILITY OF GASES IN CAPILLARY MOISTURE

When two immiscible liquids are shaken with a substance that can dissolve in both, the solute distributes itself between the two solvents, provided it is not dissociated in the one solvent more than in the other. If the water held in the minute capillaries of a porous substance is not chemically combined and is in no way different from ordinary free water beyond the expected change in its surface tension, then the distribution law should hold, and the absorbed water should be capable of dissolving out a part of the solute from an immiscible liquid.

The problem touches a wider question, namely, adsorption from solution, to which reference will be made incidentally. It is curious, however, that in the case of adsorption of gases as well as of adsorption from solution, very little attention has been paid to the moisture content of the adsorbent. It is generally not realized that water, with its labile hydrogen and hydroxyl ions, is not only a universal solvent but is extraordinarily prone to enter into loose chemical combination with a variety of substances. When water is absorbed by a capillary system, it can present an amazingly large surface, which is extremely active. It is this surface that is capable of entering into loose chemical combination with the substances, and which is the seat of adsorption - not the surface of the solid adsorbent.

This capillary water can dissolve gases, and it is no exaggeration to say that most of the experiments on adsorption of gases by solids could be accounted for much more satisfactorily on the basis of the solution of the gas in the capillary water. The fact that no precautions have been taken to dry the adsorbent in any of the experiments is significant, and when it is remembered how extraordinarily difficult it is to eliminate the last trace of moisture from porous substances, it is doubtful if such precautions would have been of much avail. At any rate, these experiments have created a most unhappy state of affairs. The capillary-condensation theory of moisture absorption has been rejected on the ground that gases are absorbed by solids which could not possibly condense in the pores.

Before this view is accepted it must be proved definitely and conclusively that the absorbent is free from every trace of moisture. It is the author's contention that the moisture goes in first, the gas following as a matter of course, and that an absolutely dry substance will not adsorb an absolutely dry gas. The moisture, therefore, may constitute the hook or peg on which a gas may hang in a capillary system. It is unfortunate that the word "adsorption" or "sorption" has a universal application, and that two phenomena which may have nothing in common have come to be regarded as similar. For instance, if the solution of a substance in a water-immiscible solvent is shaken with an absorbent containing moisture, a part of the solvent may be removed purely in accordance with the well-known distribution law; yet the phenomenon will have all the appearance of adsorption from solution, and we shall be talking of adsorption by the solid substance, which may do nothing more than hold the moisture in its pores and thus impart to it an enormous surface.

Silica is by far the most appropriate substance for these studies. Apart from the fact that it has an enormous surface and can absorb large amounts of moisture, it is quite unreactive toward acids, and a number of organic acids that are soluble both in water and organic solvents could be studied.

An extensive investigation of the adsorptive properties of hydrated silica has been carried out by Patrick and his co-workers. They have studied the adsorption of gases and vapors, of NaOH from water solution, and adsorption from organic liquids. They have also studied heat of wetting and heat of adsorption in the silica, as well as the displacement of water from the hydrogel by other liquids. The latter was also studied by Firth and Pinse. Adsorption with quartz and with silica which had been ignited for a long time was studied by Jones, Joseph and Hamcock. Silica gel containing about 8.5% water has been used in adsorption studies by Mukherjee and his co-workers. A good deal of accurate work has been done by Bartell and Yingfu on the adsorption of alkalies and acids. Patrick and his co-workers studied adsorption in organic liquids immiscible with water and thus created just the right conditions for the distribution of the solute between two immiscible liquids without recognizing its importance.

Silica used in this investigation was prepared in the usual way by precipitating from sodium silicate by the gradual addition of dilute HCl under violent stirring. The resulting silica gel was washed free of salts and dried. It was then washed with hot dilute HCl and then with water until the wash water was free from Cl ions. Silica thus prepared did not adsorb any acid from water solution or organic solvents miscible with water; but it could adsorb organic acids from solvents immiscible with water in a manner that could be explained only on the basis of the distribution law.

Before starting experiments with capillary water and some im-

miscible liquid it was considered desirable to study the effect of changing the vapor pressure of water on this distribution. For this purpose H_2SO_4- water mixtures were chosen, as with these the vapor pressure can be varied at will. Benzene was used as the immiscible liquid and benzoic acid as the solute. 20 cc of pure benzene were shaken (intermittently with hand) with 20 cc of H_2SO_4-water mixtures of relative humidity ranging from 10 to 99%. In one experiment 0.2 gram and in another 0.8 gram and in another 0.8 gram of benzoic acid was used. The experiment was conducted in a thermostat maintained at 20°C. After half an hour the bottles were taken out and the amount of benzoic acid in the benzene layer determined by titration with N/40 NaOH. It was found that the lowering of the vapor pressure of water had no effect on the distribution, and the results were similar in all cases to those with pure water.

In the first instance preliminary experiments were carried out with a sample of air-dry silica, by shaking it for varying lengths of time with a solution of benzoic acid in benzene. It was found longer shaking, up to one hour, had no effect. This is not surprising in view of the enormous surface of capillary water.

A number of organic solvents and a few acids were next tried. Two grams of silica containing 11.0% moisture were shaken with 20 cc of the liquid for half an hour; 10 cc of the supernatant liquid was taken for titration. In the results recorded in Table 89, C_0 represents the initial concentrations of the solute in millimols per litre, C its final concentration, and A the amount in millimols adsorbed by 100 grams of silica.

It will be noted that the recording of the results follows more or less conventional lines, though it is not the silica which is the real adsorbent. Adsorption of benzoic acid in benzene has been studied at different concentrations and the results, when plotted, can be fitted into some sort of adsorption isotherm. This is merely illustrative of the fact, already well known, that the existence of an adsorption isotherm is no proof of adsorption. The fact that there is practically no adsorption from water or liquids miscible with water is proof that there is no adsorption on the surface of the solid. Of course some may still choose to call it adsorption on the surface of water of the Gibbs - Thomson type, especially as it is confined to the interface. For the present, however, we are not concerned with the mechanism of this adsorption, but merely with the fact that the real adsorbent is the capillary water, which itself is not adsorbed in any mysterious way but merely held in minute capillaries by virtue of which it has acquired enormous surface.

Having established that the capillary water is the real adsorbent, we can now vary the moisture content, corresponding to different humidities, and consequently have the absorbent water in capillaries of a varying limiting size. The silica used for these experiments was dried at 250°C. It still retained 11% moisture which could be

driven out only by heating to 900°C. This moisture, however, is not included in the results, and the sample dried at this temperature is considered to be at zero humidity and zero moisture content, though it actually contains about 11% water.

It is found that when the last traces of moisture are removed from silica the entire capillary structure breaks down, and even

TABLE 89. Adsorption of various substances from different solvents by silica.

(1) Benzoic acid

Co	C	A
Benzene		
0.132	0.075	17.1
0.199	0.137	21.6
0.272	0.187	25.5
0.329	0.239	27.0
0.391	0.295	29.0
Xylene		
0.142	0.060	19.1
Toluene		
0.144	0.050	21.9
Chloroform		
0.131	0.085	10.8
Carbon tetrachloride		
0.157	0.014	33.4
Ether		
0.291	0.287	1.3
Water		
0.142	0.135	1.6
Methyl alcohol		
0.142	0.142	0
Ethyl alcohol		
0.130	0.130	0
Acetone		
0.130	0.127	0.077

(2) Salicylic acid

Co	C	A
Benzene		
0.08	0.035	18.0
Chloroform		
0.240	0.176	16.0
Water		
0.070	0.055	1.8
Methyl alcohol		
0.140	0.140	0
Ethyl alcohol		
0.160	0.160	0
Acetone		
0.130	0.130	0

(3) Phenyl acetic acid

Co	C	A
Benzene		
0.0775	0.0275	20.0
Toluene		
0.079	0.035	17.6
Xylene		
0.100	0.060	16.0
Chloroform		
0.099	0.075	9.6
Carbon tetrachloride		
0.095	0.019	30.4

Water, methyl, and ethyl alcohol, acetone: No adsorption.

Co: Initial concentration millimoles per liter.
C : Final concentration millimoles per liter.
A : Amount of solute adsorbed in millimoles per 100 g of silica.

water is not absorbed. This happens when silica is ignited at 900°C, or the moisture is driven out by heating for 48 hours in a vacuum at 120°C. The silica used in these experiments after drying at 250°C was brought into equilibrium with atmospheres of different humidities by keeping over H_2SO_4- water mixtures in desiccators for several days. The moisture absorbed in every case was recorded as percentage on the dry weight. Three observations were taken in each case, the time of contact varying from 1 minute to 18 hours. The results are given in Table 90.

On the face of it one would have expected greater adsorption at

higher moisture contents; but the results actually show the reverse. If the adsorption of water had occurred in monomolecular layers by residual chemical forces we should have expected the same value for adsorption at all humidities; but if it is due to capillary condensation, then naturally at lower humidities when it is held in smaller capillaries, the exposed water surface is larger than when capillaries of a larger diameter come into play.

As has been shown before, the vapor-pressure curve is a reflection of the size distribution of particles, and at higher humidities when the interstices between the larger particles are filled, those between the smaller particles are simply swamped with water. We can perhaps visualize the actual state of affairs better if we fix our

TABLE 90. Adsorption of benzoic acid from benzene by silica with varying moisture content.

Humidity (%)	Moisture (%)	Co	C	A	Time of contact
99	76.2	0.281	0.250	12.4	1 minute
	75.0	0.310	0.262	11.9	30 minutes
	74.5	0.312	0.272	10.0	18 hours
90	38.3	0.281	0.232	19.6	1 minute
	41.5	0.310	0.232	19.3	30 minutes
	37.6	0.281	0.235	19.3	18 hours
70	23.8	0.281	0.218	25.2	1 minute
	24.0	0.310	0.205	25.6	30 minutes
	23.5	0.312	0.210	24.4	18 hours
50	15.1	0.281	0.213	27.2	1 minute
	15.0	0.310	0.200	27.5	30 minutes
	16.0	0.312	0.205	26.8	18 hours
30	11.8	0.281	0.209	28.8	1 minute
	12.5	0.310	0.200	27.5	30 minutes
	11.3	0.312	0.195	28.8	18 hours
10	5.8	0.281	0.201	32.0	1 minute
	6.7	0.310	0.180	32.5	30 minutes
	6.0	0.312	0.187	30.8	18 hours
0	0	0.281	0.261	8.0	1 minute

Co: Initial concentration in millimoles per liter.
C : Final concentration in millimoles per liter.
A : Amount of solute adsorbed in millimoles per 100 g.

attention on a triangular space between three spheres. When the space is full of water the surface is minimum. As the water evaporates the exposed surface of water increases until the pendular stage is reached, when it suddenly decreases as the continuity of the water film is broken. Henceforth, the surface decreases until a state of complete dryness is reached.

This is exactly what happens in the case of adsorption. At the highest humidity the surface exposed is minimum, and so is the adsorption. As the silica dries more and more, adsorption increases correspondingly until a state of dryness is reached. At this point water films exist as discrete rings; adsorption then drops abruptly, reaching a value in the neighborhood of zero when the entire quantity of water has evaporated.

This view brings us into partial conflict with the idea of partition coefficient between two immiscible liquids which we were trying to introduce into the line of argument. However, a moment's reflection will make it clear that the conflict is purely superficial, for partition coefficient is essentially a phenomenon associated with the interface. It is perfectly true that when two immiscible liquids are brought into contact without mixing or shaking, the equilibrium is confined to the interface. It is because the area of the interface is so small that ordinary analytical methods fail if confined to the interface alone. The object of shaking is twofold: to increase the area of the interface, and by continuously exposing fresh surfaces eventually to attain a state which amounts to having monomolecular layers of the two liquids lying flat against each other. Thus without going into the question as to how deep is the influence of the interface, even a monomolecular layer of water on a surface would be capable of adsorbing from an immiscible liquid.

The fact that equilibrium is attained almost instantaneously confirms the view that adsorption is confined to the interface, and that there is no diffusion into the body of the liquid held in the capillaries. It is not unlikely that the solute molecules are oriented at the interface and exist partly in the water and partly in the other liquid.

In order to see if water held by salt hydrates would show similar behavior, a dilute solution of $CuSO_4$ was added to alcohol which was kept violently stirred. A very fine precipitate of $CuSO_4 . 5H_2O$ was obtained, which it was hoped will have a large surface. Adsorption of benzoic acid in benzene was studied with this, exactly as in the case of silica. There was absolutely no adsorption. The experiment was repeated with $Na_2SO_4.10H_2P$ prepared in the same manner. There was no adsorption in this case.

In the discussion of the absorption of moisture by dehydrated salts, it was pointed out that the essential difference between salt hydrates and capillary and porous bodies is the nature of the capillaries, which in salt hydrates is so constituted that the actual surface exposed is extremely small. On that basis alone any adsorption of a solute from an immiscible liquid will be ruled out. Evidently the method of reducing the salt hydrates to a fine state of subdivision by precipitating them in alcohol is not very effective. It may still be possible to reduce a salt hydrate to colloidal dimensions and study the adsorption with an immiscible liquid. In any case even if we suppose that adsorption with salt hydrates does not occur because water is chemically held, we are still left with the inevitable conclusion that water in silica must be held differently down to the last traces.

As has been stated before, the adsorption of gases by solids has been studied extensively without recognizing the importance of moisture that may be present in the adsorbent. During the researches on the subject the experimental technique has been brought to perfection. The author started with the primary object of studying the

solubility of gases in the absorbed water; the choice of gases and the technique was perforce restricted and specialized. Of the gases, CO_2, SO_2 and H_2S appeared to be suitable on account of their appreciable solubility and ease of estimation by chemical methods. Gels of silica and alumina were chosen as absorbents for their high absorptive power for water. All three gases were used with silica, but with alumina only the absorption of CO_2 was studied, as it was feared that there may be some chemical reaction between the other gases and alumina.

Gels of silica and alumina were prepared in the usual way by precipitating from sodium silicate and $Al_2(SO_4)_3$ with HCl and ammonia, respectively, under violent stirring, followed by thorough washing with distilled water. Several samples of both silica and alumina were dried at various temperatures; this gave a series of capillary systems similarly constituted, but differing in absorptive capacity. These will be referred to as Si and Al with the numeral following indicating the temperature to which it has been heated; for instance Si 250 represents the sample of silica heated to 250°C. Similarly Al 450 indicates a sample of alumina heated to 450°C.

Five grams of each of the gel samples were spread out in petri dishes and placed in desiccators over H_2SO_4- water mixtures, giving appropriate humidities. After a week, when equilibrium with moisture had been attained, the gas was let in and the air swept out. The desiccator was then closed. The sample was kept in contact with the gas for 24 hours, the gas being renewed after every eight hours. After the equilibrium had been established in each case, the samples were boiled with CO_2-free water, using a Kjeldal trap into standard baryta in the case of CO_2, and into iodine solution in the case of SO_2 and H_2S. Control experiments were run in each case. From the known weight of moisture absorbed by each sample from the various humidities the volume of the gas dissolved in 1 gram of the capillary moisture was computed. It was of course assumed that the dissolved gas is uniformly distributed in the entire body of the absorbed water; though this may not be the case, it will not effect the line of argument. In Table 91 are given the moisture contents of the various samples in equilibrium with different humidities. It will be seen that at 900°C the capillary structure of silica is completely broken down and that there is no absorption of moisture at any humidity after the sample has been subjected to this temperature. At lower temperatures there is a progressive decrease in its absorptive capacities which can be accounted for only by a progressive fusion of the particles, the process being complete at 900°C.

The volume of each gas at N.T.P. absorbed per gram of water held in each sample was computed from the total amount of gas taken up by a known weight of the sample and its moisture content. The results are given in Table 92. It will be seen that, as in the case of solution, adsorption decreases with increase in moisture

content, and similar arguments would apply as well in this case to account for this behavior. Whether we say the gas is adsorbed or dissolved in the capillary water is immaterial for the present; but

TABLE 91. Moisture absorption by silica and alumina heated to different temperatures from atmospheres of various humidities.

Sample No.	Percentage absorption of moisture from various humidities						
	10%	30%	50%	70%	90%	97.6%	99.9%
Si 250	6.02	18.42	28.1	35.6	40.2	45.4	46.62
Si 450	2.68	7.12	13.26	24.2	33.62	37.8	38.2
Si 650	1.44	2.80	4.60	8.2	13.6	16.0	16.4
Si 800	0.32	0.68	1.46	2.18	2.62	3.04	3.12
Si 900	0	0	0	0	0	0	0
Al 250	8.48	23.1	30.6	38.6	46.0		53.6
Al 450	3.92	12.1	16.22	28.64	34.2		40.46
Al 650	0.68	1.44	3.26	6.4	8.96		10.42

TABLE 92. Volumes of various gases absorbed per gram of capillary water held in samples of silica and alumina.

Sample No.	cc of gas absorbed per gram of water held at different humidities						
	10%	30%	50%	70%	90%	97.6%	99.9%
				Carbon dioxide			
Si 250	25.61	20.26	18.46	10.45	5.76	2.90	2.43
Si 450	23.24	18.47	16.53	12.28	4.80	2.42	2.60
Si 650	25.6	20.12	19.12	9.12	5.42	2.68	2.10
Si 800	25.0	18.68	15.00	10.20	5.16	3.12	2.40
Al 250	28.43	23.47	21.10	14.64	7.25		2.52
Al 450	30.10	24.0	20.24	15.00	6.82		2.68
Al 650	31.64	24.12	18.08	13.83	7.45		3.04
				Hydrogen sulfide			
Si 250	28.24	20.13	11.34	7.26	4.06		2.12
Si 450	27.60	18.02	13.16	6.42	4.92		1.99
Si 650	27.20	18.80	13.00	8.10	4.00		2.02
Si 800	27.32	19.42	10.48	7.64	3.82		1.12
				Sulfur dioxide			
Si 250	124.62	70.46	51.64	45.26	18.62		9.22
Si 450	118.47	64.28	54.24	42.10	19.00		10.14
Si 650	120.26	68.16	53.10	42.24	19.24		10.32
Si 800	126.19	70.0	50.02	42.16	18.80		9.68

it is important to know whether it is confined only to the surface of the water, or whether the gas had penetrated deeper into the capillary layers. In view of the extremely low rate of diffusion of a gas in water, it is perhaps more correct to assume that the gas is taken up only by the molecules of the exposed water surface. In any case,

the results obtained can be accounted for only by the view that the surface of the water interface decreases as the moisture content increases, which could happen only if the water was held in capillaries and did not exist as mere polymolecular films, though at very low humidities the possibility of monomolecular films is not ruled out. We do know, for instance, that moisture held at 4-5% humidity is just enough to give a monomolecular layer on the total surface presented by the solid adsorbent. Whether at that stage the water still chooses to occupy the isolated capillaries or spreads out on the entire surface, is more than one can say; but we must remember that at one stage we shall be forced to regard the surface tension forces that are responsible for capillary condensation as identical with the residual valencies which cause monomolecular adsorption.

TABLE 93. Volume of CO_2 absorbed per gram of alcohol held in samples of silica and alumina.

Sample No.	cc of CO_2 absorbed per gram of alcohol at different humidities			
	28.14%	47.56%	76.13%	91.2%
Si 250	29.20	24.12	13.40	8.46
Si 450	28.62	22.68	14.22	10.12
Si 650	30.48	24.32	14.20	8.26
Si 800	30.00	23.84	13.92	9.42
Al 250	34.12	24.20	15.26	11.10
Al 450	32.04	25.16	16.00	10.42
Al 650	34.16	22.28	16.12	12.00

In order to show that the phenomenon of adsorption of gases by capillary water is of a general character, alcohol was substituted for water. Alcohol-glycerin mixtures giving different relative vapor pressures of alcohol were prepared, and the experiment on absorption of CO_2 was repeated exactly as in the case of water (Table 93). It is clear that the general run of results is in no way different from those with water. However, CO_2 is absorbed more than in water at corresponding humidities. This is consistent with the fact that CO_2 is more soluble in alcohol than in water at the same pressure. Solubility, therefore, must play an important role in these experiments, even if adsorption is confined to the surface. If surface tension played the dominant role we would have expected a lower absorption of CO_2 for alcohol. Another method of throwing light on this question would be to study the absorption of CO_2 in capillary water at different temperatures. As temperature has very little effect on the surface tension of water, but a very great effect on the solubility of gases, the magnitude of the differences in absorption will decide whether the phenomenon is due to solubility or to adsorption of a sort.

For this study soils were used instead of silica, partly with the object of confirming the previous results with a substance of diverse nature. A few typical soils were selected. Some of their single-

value constants are given in Table 94, and moisture content - vapor pressure relationship in Table 95. The soils were first leached with 0.05N HCl and then with water, the final washing being given by alcohol before drying in an oven at 100-110°C. Forty-gram portions of the oven-dried soils were brought into equilibrium with atmospheres of different humidities in desiccators, followed by exposure to CO_2 gas for 24 hours. The amount of CO_2 absorbed was determined as before by adsorption in standard baryta.

TABLE 94. Single-value constants of soils used for CO_2 absorption.

Soil No. P.C.	Exchange capacity (m.e./100 g)	Clay (%)	pH
6	27.7	31.4	5.29
13	50.0	60.3	8.53
153	48.6	25.9	7.48
167	11.0	16.9	6.47
202	18.0	20.10	8.37
227	16.5	10.40	7.01
233	26.6	37.2	8.28
296	25.6	11.65	8.65

TABLE 95. Moisture absorption of soils from atmospheres of different humidities.*

Soil No. P.C.	% Moisture absorption from atmospheres of different humidities							
	10%	30%	50%	70%	90%	96%	97.7%	99%
6	0.46	0.57	1.46	2.17	3.76	4.50	4.83	5.49
13	1.77	3.7	9.57	12.97	18.02	20.79	-	21.31
153	0.49	0.60	1.35	1.94	2.08	2.34	2.77	2.84
167	0.46	0.60	1.11	1.61	1.74	2.17	-	2.34
202	-	0.80	1.66	2.29	3.10	3.47	3.39	3.67
227	0.52	0.70	1.12	1.68	1.99	2.18	2.20	2.48
233	0.90	1.95	4.23	5.49	7.16	9.17	-	10.09
296	0.40	0.57	0.76	1.67	1.46	1.94	2.02	2.31
212	0.53	0.68	1.26	2.43	-	3.42	-	3.90

* Moisture absorption determined after acid treatment and leaching.

Experiments were conducted at three different temperatures, viz., 0, 20 and 40°C. During moisture and CO_2 absorption the desiccators containing soils were kept in an ice bath for observations at 0°C and in incubators maintained at the requisite temperature for observations at 20 and 40°C. The results, given in Table 96, bring out clearly the enormous effect of temperature on absorption of CO_2. As in the case of silica and alumina, absorption per gram of capillary water at a particular humidity and temperature is constant, irrespective of the nature of the soil. It therefore appears highly probable that CO_2 absorbed by soils in nature is in reality dissolved in soil moisture. If this view is correct, dry soil should not absorb any CO_2 at all.

To verify this point tests were made on dry soils. One portion of each sample was dried in an air oven at 110°C and the other at 200°C in a current of dry air. The amounts of CO_2 taken up by 40 grams of dry soil are given in Table 97, along with the amounts taken up by the same soils in equilibrium with 10% humidity. There is appreciable absorption in soil dried at 110°C, especially at 0°C. This is not surprising in view of the fact that it is impossible to expel

TABLE 96. Volume of CO_2 (at N.T.P.) absorbed by 1 gram of capillary water held in soils at various humidities and temperatures.

Soil No. P.C.	Temperature 40°C — cc of CO_2 absorbed by 1 g of capillary water at various humidities					
	10%	30%	70%	90%	96%	99%
6	36.26	9.38	7.71	6.31	6.01	4.96
13	44.71		11.10	8.50	6.41	5.38
153	40.08	11.24	9.34	7.36	6.47	3.93
167	37.50	9.16	9.09	5.57	6.60	3.56
212	39.54	11.27	10.33	6.60	5.19	4.29
227	41.51	12.82	10.76	5.60	5.43	3.91
233	45.04		10.95	6.74	6.64	5.47
296	36.25	9.67	10.87		4.31	3.30
Average	40.12	10.59	9.63	6.67	5.40	4.35
	Temperature 20°C					
6		20.66	10.94		11.44	10.06
153		23.06	10.43		10.18	9.62
167		23.15	10.40		9.94	8.37
202		23.38	11.87		11.90	11.23
227		22.90	12.00		10.23	9.55
296		22.05	11.24		10.46	8.76
Average		22.53	11.06		10.69	9.60
	Temperature 0°C					
6	69.71	53.46	23.57		23.21	20.64
153	73.10	56.59	22.69		20.98	20.99
167	73.70	56.81	23.01		21.57	19.40
212	73.84	56.0	24.74		23.57	20.67
227	72.43	56.70	24.47		21 13	19.68
296	69.85	51.37	24.20		21.26	19.04
Average	72 10	55 15	23.78		21.95	20.07

the last traces of water by heating the soil at 100-110°C. It is also not unlikely that at 0°C some moisture is taken up by the soil, as no special precautions were taken to exclude it rigidly.

From the foregoing it may be concluded that the gases absorbed by porous substances are not condensed as such in the capillary spaces, but are dissolved in the capillary-condensed liquid. The fact that most of the gases usually taken up by silica, charcoal, etc., from the prevailing atmospheres are easily liquefiable has led to the common belief that they are condensed in the capillary spaces.

TABLE 97. Absorption of CO_2 by soils dried at 100 and 200°C.

Soil No. P.C.	cc of CO_2 absorbed by 40 g soil at 0°C		cc of CO_2 absorbed by 40 g soil at 40°C		
	Dry soil 100°C	In equilibrium with 10% humidity	Soil dried at 100°C	Soil dried at 200°C	In equilibrium with 10% humidity
6	5.86	12.85	1.38	0.44	6.79
153	3.06	14.25	1.38	0	7.81
167	4.45	13.69	0	0	6.97
212	3.06	15.65	0	0	8.37
227	2.69	15.09	0.82	0	8.65
296	3.06	11.45	0.54	0	5.85
233			0.82	0	16.21
13			2.82	0	31.61

But it is significant that these very gases are soluble in water, and therefore are likely to be taken up by the capillary-condensed water.

CHAPTER XIV

INFLUENCE OF SALTS ON MOISTURE ABSORPTION BY SOIL

The presence of soluble salts in soils is known to affect their hygroscopicity to a marked extent. The difference becomes appreciable at a certain critical humidity which corresponds to the vapor pressure of the saturated solution of the salt. This indicates that capillary moisture is as good a solvent for salts as water in bulk. Some years ago, following the work of Bouyoucos and his co-workers, there was a good deal of controversy over the question of "unfree water" in soils. It originated from the observations of Bouyoucos that freezing-point depression of moist soil increased in geometric progression as the moisture content decreased in arithmetic progression. At that time it was supposed that the freezing-point depression of moist soils was due to salts dissolved in the soil water. It was not realized that lowering of the vapor pressure of water when held in capillaries is thermodynamically related to decrease of its freezing point or rise in its boiling point. The whole controversy, though based on wrong assumptions, resulted in some useful work, which has a bearing on the present discussion. It was very pertinently argued that if the capillary water in the soil was "unfree", in the sense that it was not available for dissolving any soluble material, then it should be possible to extract a certain amount of water from a solution by adding dry soil to it. Numerous experiments designed to elucidate this point gave negative results.

Keen, who subjected Bouyoucos' data to a comprehensive mathematical analysis, concluded that if the abnormal freezing-point depression of soils at low moisture content was due to a part of the water being "unfree", then the quantity of water thus rendered unfree must vary with the total moisture content. This will be clear from Table 98, wherein are recorded the results of lowering the freezing point of a clay soil at different moisture contents (examined by Bouyoucos). The theoretical freezing-point depression has also been calculated, assuming the inverse proportionality law to hold good. From the theoretical and actual values of freezing-point de-

pression, the amount of unfree water has been calculated. Thus to account for abnormal freezing-point depression we have not only to postulate the existence of unfree water, but to suppose that its amount must vary with the moisture content.

Later, Bouyoucos developed another method for finding the amount of unfree water, which he called the dilatometer method. The principle of this is based on the fact that water expands on freezing; knowing the coefficient of expansion of water on freezing and also the total water content of a soil, the amount of water that freezes (free water) and does not freeze (unfree water) can be calculated.

TABLE 98. Lowering of the freezing point of a clay soil at different moisture contents, with the calculated unfree water (Bouyoucos).

Moisture content (%)	Theoratical F.P.D.	F.P.D. found	Calculated unfree water (%)
34	0.034	0.034	
32	0.036	0.042	4.5
30	0.039	0.062	11.1
28	0.041	0.082	14.0
26	0.044	0.127	17.0
24	0.048	0.212	18.56
22	0.053	0.307	18.21
20	0.058	0.580	18.00
18	0.064	0.922	16.75

The moist soil is held in a dilatometer filled with ligroin and frozen at different degrees of super-cooling. For classifying the moisture into various forms the following principle was observed: All the water in the soil that freezes at or slightly below 0°C is considered free water, because pure water in mass is known to freeze at this temperature. All the water that freezes from this temperature down to -78°C is regarded as capillary-absorbed water; while all the water that fails to freeze is considered unfree water. With this technique Bouyoucos found that the amount of water which soils are able to render unfree does not vary with the moisture contents, but appears to remain constant.

This discrepancy between the results of the freezing-point depression and the dilatometer methods leads to two alternatives: either the abnormal freezing-point depression is due partly to unfree water, which is constant, and partly to an unknown factor, which is variable; or the unfree water that causes the abnormal freezing-point depression is not identical with the unfree water that fails to freeze even at -78°C. In view of the importance of the contact angle in determining the entry of liquids into minute capillaries it would not be surprising if a liquid like ligroin failed to wet some of the smallest capillaries. Thus the water held in them, even if it did freeze, would show no corresponding change in the volume of the ligroin with which the dilatometer is filled.

The dilatometer method is defective in another respect too, namely, that it depends on the assumption that the change in volume of water on freezing is the same when it is held in minute capillaries as in bulk. This may or may not be true. It must be remembered that in view of surface-tension forces, the surface film of a liquid a few molecules in thickness may be compressed. This would make no difference in the density of the liquid in bulk, but when it is spread out so as to expose a surface which is large compared to its mass, then the total mass might behave as a denser liquid, as if it were compressed. In this condition the change in volume on freezing may be quite different from that of the liquid in bulk.

Parker in a series of papers arrived at the following conclusions:

(1) That a much greater increase in the freezing-point depression of soils with decrease in moisture content than indicated by the law of inverse proportion is due to the solid material, and not to the existence of unfree water, which would cause a greater concentration of the soil solution. This was supported by experimental evidence, where it was shown that solid material caused a depression of the freezing point of water, benzene and nitrobenzene in the film or capillary condition.

(2) Alcohol and glycerin solutions are not made more concentrated when added to dry soil, as would be the case if part of the water were rendered unfree by the soil. Therefore, all the water must act as a solvent and exist in the liquid condition.

(3) It is possible to displace part of the soil solution from a soil, the moisture content of which is less than that of the unfree water.

The evidence adduced by Parker against the hypothesis that a part of the water in soils is inactive or unfree, i.e., does not act as a solvent seems to be fairly conclusive. However, McCool and Weidemann later showed that when soil was added to sucrose solution it extracted some water, leaving the solution more concentrated. By measuring the increase in concentration of molar sucrose solution when brought into contact with different soils and soil separates by the freezing-point method, they found that some organic soils could render as much as 26 to 35 per cent of the water unfree.

They have also recorded some experiments on the increase of concentration of potassium in KCl solution when brought into contact with soils. This result is similar to that obtained in an earlier work by McCall, Hildebrandt and Johnson, who noticed negative adsorptions in the case of potassium. These results, however, cannot be cited in support of the hypothesis of unfree water, as sufficient attention was not paid to the phenomenon of base exchange and the distribution equilibrium between the soil and the solvent.

Sucrose on the other hand does not react with soil and is not absorbed by it; therefore, the results obtained with this substance are of considerable interest, because if the increase in concentration of the sucrose solution as measured by the freezing-point method cannot be accounted for in any other way, then not only is the hy-

pothesis of unfree water substantially correct, but we are provided with a simple means of measuring the capacity of soils for rendering water unfree. It seems, however, that these workers overlooked one important factor, namely, the possibility of inversion of sucrose by the soil, which will result in a lowering of the freezing point and causing the solution to appear as if it has become more concentrated. That such inversion does take place has been shown conclusively (Part I, Chapter VI).

Two factors have been shown to be important in this connection - the acidity of the soil and the temperature. The authors themselves showed that considerably more water was removed by organic soils (higher acidity) than others, and much more so when the samples were maintained at a temperature higher than that existing in the laboratory. This was evidently due to the enhanced rate of inversion at higher temperatures. It was, therefore, decided to study this phenomenon, using sugar solutions of varying concentrations and under conditions that precluded the possibility of the results being vitiated by inversion.

TABLE 99. Soils used for F.P.D. experiment.

Soil	Clay (.002-mm) (%)	Hygroscopicity at 50% humidity (%)
Gonri (Pusa)	43.6	2.65
Montgomery	73.0	4.06
Hoos Field (Rothamsted)	35.2	3.37
Akola (black cotton soil)	60.6	10.00

Four soils were examined for this purpose. These are given in Table 99, along with their clay content and moisture absorption at 50% humidity. The soils were first freed from all soluble salts and replaceable bases by exhaustive treatment with 0.05N HCl, followed by prolonged leaching with water. After treatment the soils were dried over sulphuric acid in vacuum desiccators. The Beckmann technique of determining the freezing point was used to study the changes in concentration.

To 25 cc of redistilled water varying amounts of pure sucrose were added and the freezing points noted; 25 grams of dry soil were then quickly added and the freezing point again noted. A change in the freezing point was a measure of the change in concentration. Equilibrium was attained in about 15 minutes and was noted when three consecutive readings agreed within 0.002°C; as a rule the agreement was even better. To prevent inversion of sucrose by soil, it is important that the temperature of the mixture should never be allowed to rise above 5 to 6°C. At this low temperature no inversion was noticed even after 24 hours.

The results given in Table 100 show that up to a concentration

ranging from about 4 to 8%, depending on the nature of the soil, the latter is able to absorb the sugar solution as such. From concentrations higher than a certain minimum the soil evidently takes up a solution of a weaker concentration, the amount of which is more or less constant for a given soil.

The figures in brackets indicate the percentage of sugar solution of a weaker concentration absorbed by the dry soil (x). These have been calculated by the formula:

$$x = 4\left(25 - \frac{25(F-F')}{(F-F') - (L-L')}\right)$$

Where F = freezing point of sucrose solution

F' = freezing point of sucrose solution which the soil can absorb as such (i.e., the point of intersection of the two portions of the curve obtained by plotting the concentration of sugar solution as abscissa, and freezing-point depression as ordinate).

L = freezing-point lowering produced in the solution by soil.

L' = freezing-point lowering produced in water by soil.

TABLE 100. Change in the freezing-point depression of sugar solutions due to the addition of 25 g of dry soil.

Gm of sugar added to 25 cc of water	F.P.D. (°C)			
	No. 1	No. 2	No. 3	No. 4
0	0.010	0.010	0.011	0.008
0.5		0.010	0.010	0.008
1	0.010	0.010	0.010	0.011
2	0.012	0.010	0.011	0.032(9.92%)
3	0.012	0.018(4.84%)		0.061(10.72%)
4	0.013	0.030(4.88%)	0.029	0.090(10.88%)
5	0.011	0.041(4.72%)	0.041	0.117(10.64%)
6	0.015	0.052(4.44%)	0.050	0.142(10.28%)
8	0.018		0.069	0.195(10.04%)

The phenomenon noted in the case of sugar solutions might be due to a critical molecular association of the sugar and water molecules, and the limiting size of the capillaries that are responsible for moisture absorption. The results, however, leave no doubt that moisture held in the capillaries is as good a solvent as water in bulk. The fact that highly concentrated sugar solution is not absorbed as such rather supports the capillary theory, according to which a purely physical hindrance to the entry of associated molecules of water-sugar is conceivable.

By using 0.05N and 0.1N solutions of chlorides and nitrates of potassium and sodium, the author found no change in concentration of nitrate or chloride ions when shaken with a dry soil which showed

the highest negative adsorption in sugar solutions. Before shaking with these salt solutions the soil was converted into potassium and sodium saloids, respectively, so that there was no interference from base exchange. The values for sugar solution absorption run parallel to those for water absorption at 50% humidity, and bear no relation to the clay content (Table 99). As a matter of fact, by a strange coincidence they are almost equal to moisture absorption at 50% humidity. Soil No. 1 shows very little effect.

The fact that the moisture absorbed by soils acts as a solvent is a strong argument in favor of the capillary condensation theory. Not only is the capillary moisture capable of dissolving salts, but the hydration and dehydration of salts goes on normally in the minute capillaries. A notable example of this phenomenon is that of Na_2SO_4, which is normally present in saline soils. It forms a number of hydrates, of which the deca-hydrate ($Na_2SO_4 \cdot 10H_2O$) is the most important. This hydrate occupies 82.5% more space than the anhydrous salt. When this enormous increase in volume takes place in minute capillaries the results are disastrous for the entire structure. The capillaries are ripped open and even the hardest stones crumble into powder. The critical humidity for the formation of the hydrate is about 80% and critical temperature about 32°C. Therefore, if the temperature or humidity alternates above and below these critical points, the structure is bound to fall to a powder. The practical importance of this phenomenon is obvious.

At higher humidities the change in hygroscopicity of the saline soil is so phenomenal that it cannot be mistaken. At lower humidities the change, if any, must be ascribed to surface-tension effect and therefore must support the capillary condensation theory. The choice of the proper salt for studying the effect of changes in surface tension on hygroscopicity is rather restricted in view of the slight effect on surface tension produced by most of the common salts. Sodium stearate has certain advantages in this connection. In spite of its limited solubility it has an appreciable effect on surface tension. Besides, unlike other salts, it does not crystallize out from water, and thus a more uniform distribution is insured. Another advantage of this salt is that very little moisture is taken up by it, even at humidities as high as 90%; therefore the effect on the vapor pressure of the capillary system containing it is purely due to the lowering of the surface tension of the capillary water.

Nine typical soils were selected for this experiment. Two 10-gram portions of the various soils 10 cc of 1% sodium stearate solution were added, and the resulting pastes, after being well and uniformly mixed, were dried first in the air and then over concentrated H_2SO_4 in a desiccator. Two-gram portions of the "salted" soils were kept over atmospheres of different humidities and the percentage moisture absorption based on the weight of the dry soil was determined. The amount of sodium stearate present in each soil was more than sufficient to give saturated solutions with water picked up from at-

mospheres of varying humidity up to 90%. The results of moisture absorption - vapor pressure relationships in soils with and without sodium stearate are given in Table 101. If sodium stearate did not dissolve in the capillary moisture, the values for equilibrium moisture content would be the same with and without the salt. The differences, however, are appreciable and in the direction expected. This will be clear from the following discussion.

TABLE 101. Humidity-moisture content relationship of soils without any salt (i) and in the presence of sodium stearate (ii a and ii b), determined and corrected values respectively.

Relative humidity (%)	Equilibrium moisture content of various soils with and without salt							
	P.C. 6	P.C. 13	P.C. 123	P.C. 154	P.C. 167	P.C. 212	P.C. 227	P.C. 296
10 (i)	0.43	2.50	1.39	0.64	0.25	0.34	0.35	0.40
(ii a)	0.34	1.90	0.95	0.22	0.20	0.27	0.29	0.26
(ii b)	0.40	2.30	1.15	0.32	0.22	0.35	0.30	0.275
30 (i)	0.82	3.85	2.14	0.96	0.38	0.67	0.56	0.41
(ii a)	0.61	3.00	1.60	0.62	0.27	0.54	0.43	0.39
(ii b)	0.72	4.25	2.10	0.85	0.38	0.70	0.54	0.47
50 (i)	1.20	7.75	4.50	1.45	1.10	1.50	0.90	0.85
(ii a)	0.95	7.10	4.05	1.47	0.90	1.20	0.87	0.75
(ii b)	0.96	7.50	4.40	1.60	0.97	1.30	0.93	0.80
70 (i)	1.27	9.00	5.02	1.67	1.15	2.05	1.28	0.96
(ii a)	1.03	8.35	5.03	1.61	1.03	1.56	1.00	0.88
(ii b)	1.20	8.80	5.60	1.67	1.10	1.69	1.14	0.98
90 (i)	3.35	11.80	9.95	2.98	2.00	2.60	2.35	1.95
(ii a)	2.60	11.95	9.55	1.90	1.60	2.25	1.80	1.50
(ii b)	2.70	12.20	9.85	1.94	1.70	2.30	1.91	1.62

The surface tension of water is 75 dynes/sq cm, and that of a saturated solution of sodium stearate 65 dynes/sq cm. From the general relationship:

$$pF = 6.5 - \log_{10}(2 - \log_{10} h)$$

where h = relative humidity
and pF = log of height in cm to which liquid would rise in a capillary of a particular diameter, which is equal to log KT, where T is the surface tension and K is a constant that depends on the density of the liquid, which in the case of sodium stearate is almost equal to that of water.

Thus, other things being equal, the pF of a moist soil will depend on the surface tension of the absorbed liquid. Since for sodium stearate solution it is equal to 65 dynes/ sq cm, we can calculate the pF and from that the relative humidity of the soil when sodium stearate solution is substituted for water. These values are given below:

Relative humidity in water	Corresponding humidity in sodium stearate solution
10	13.6
30	35.22
50	54.83
70	73.45
90	91.20

With the help of these values we can apply a correction to the moisture content of the soil at various humidities in the presence of sodium stearate; and if the theoretical reasoning is sound, the corrected values should correspond to those obtained without sodium stearate. The corrected values have been included in Table 101 and show a marked improvement in the agreement between the two sets of values. The results, however, must be considered of a quasi-quantitative nature, as the calculations are not absolutely straightforward nor the differences so great as to make it conclusive that the data fit the theory. However, the evidence as it is supports the contention that capillary moisture does act as a solvent for salts that might be present with it in the capillary spaces.

CHAPTER XV

CHANGE IN VOLUME WITH MOISTURE ABSORPTION AND EFFECT OF MOISTURE ABSORPTION ON SOIL COHESION

The phenomenon of shrinkage in soils accompanying loss of moisture is well known. Haines, in his study of the volume change associated with variations of water content in soil, has described a method of volume measurement by displacement of mercury in a constant - volume bottle. Jennings and Peterson modified Christensen's method for friability and shrinkage measurements. Soil was turned out with a cylindrical slope which was measured at the beginning and end of drying periods. Singh and Mathur used an apparatus employing the principle of air displacement. Puri and coworkers have described an apparatus for measuring volume changes, which is extremely sensitive and was found very satisfactory for such studies.

Description of the Apparatus

The apparatus, shown diagrammatically in Fig. 55, consists of a U-tube with arms of unequal diameters (31 mm and 13 mm). The narrower arm extends to a 100-cc burette tube attached to it with rubber tubing. It has also a side tube connected to two water reservoirs by pinchcocks, so that the water level in the burette tube can be raised or lowered by opening the upper or lower pinchcock. The U-tube is filled with pure, clean mercury, and water is admitted through the side tube until the burette is filled to the top division.

The wider arm of the U-tube has a thick brass cap (also shown separately on a larger scale in the diagram) that fits evenly and has a hole on one side through which passes a thin steel rod ending in a prong. Attached to the steel rod is a fine-pointed needle. The steel rod can be raised or lowered and clamped in position with a thumbscrew. The needle point is viewed through a reading microscope and its point of contact with the mercury surface can be gauged very accurately, as the needle and its shadow can be focussed simultaneously.

The zero reading of the apparatus is taken when the needle point just touches the mercury surface and the water level in the burette tube stands near the top. The brass cap is then taken off, and soil

in the form of a ball is placed on the mercury surface and pushed down with the prong of the steel rod. The cap is then replaced in the same position. As a result of the added soil volume, the mercury surface rises. The water level in the burette tube is then gradually lowered by opening the lower pinchcock, till the contact between the needle point and the mercury surface is again just made. The fall in the water level is then proportional to the volume of the soil ball, and once the apparatus is calibrated the readings can be taken in a very short time.

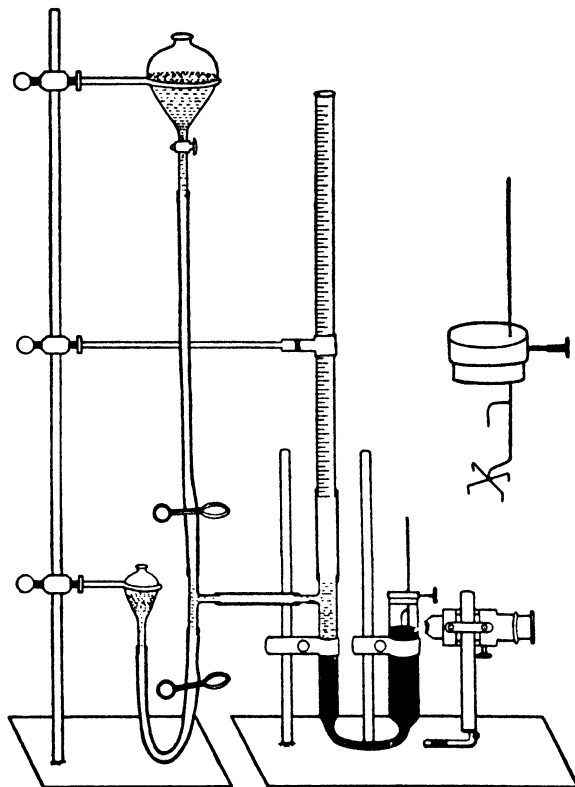



Fig. 55. Diagram of Apparatus for Measuring Soil Shrinkage
Inset: Brass cap for the wider limb of the U-tube

Calibration of the instrument is carried out by adding a known weight of mercury to the U-tube, after taking the zero reading, and noting the change in the level of the water level thus produced. The desired magnification is obtained first because the density of mercury is greater than that of water, and secondly because the diameter of the arm attached to the burette tube is smaller than the other arm. To produce a certain change in the level of mercury in the wider arm, the level of mercury in the other arm must be raised or lowered by an amount proportional to the square of the radii of the two arms.

As the magnification of the instrument can be varied by changing the ratio of the diameters of the arms of the U-tube, its sensitivity can be altered to suit individual requirements. In the instrument used, a magnification of 213 times was attained, so that a change of mercury level equal to 1 mm was shown as 21.3 cm in the burette tube. It may be mentioned that a change in temperature of 5°C produces a variation of less than 0.1 per cent in the magnification, due to the change in the density of mercury. The calibration, therefore, can be taken to be independent of temperature.

An apparatus of high sensitivity can have only a short total range, for it is not convenient to have a burette tube longer than 100 cm. Consequently it is not possible to measure volumes larger than 3 to 4 cc. For shrinkage experiments this is a decided disadvantage, as volume changes are comparatively small when the total volume has to be kept within this range. This defect is remedied by taking the zero reading with a glass ball of pre-determined volume (4 to 5 cc). This volume is added to the soil volume when readings of the latter are taken. The total volume changes due to shrinkage are then comparatively greater, since the soil volume is larger.

All the previous workers on soil shrinkage worked with high moisture contents. Typical shrinkage curves of soils consist of two parts: The first or upper portion of the curve depends on the capacity of the soil to imbibe water; it is very short or even absent in sandy soils, and may be very long in clays. The second or lower portion of the curve depends upon the pore space, since it represents the amount of water lost when the particles are most closely packed. In some soils there is a certain amount of shrinkage along this portion of the curve. Haines called it "residual shrinkage" and ascribed it to the films of colloidal material around the solid particles which form small pads between the particles, when the first stage of shrinkage has brought them into contact. It is this "residual shrinkage", which depends on the loss of hygroscopic moisture, that is our main object of study in this investigation.

Volume changes accompanying moisture absorption are well known in fibrous material possessing capillary structure. Curiously the existence of this volume change in charcoal has been used by McBain as an argument against the capillary condensation theory. His contention is that, according to the Kelvin equation, the water held in a capillary is under a negative pressure, as a result of which the walls of the capillaries tend to be pulled inward; since actually this is not the case, water cannot be absorbed by capillary condensation.

There is a fallacy in this argument, which needs clarification. The belief that water held in capillaries is under tension or compression is totally erroneous. We must remember that surface tension is purely a surface phenomenon; its influence does not extend to more than a few molecules deep into the body of the liquid. If this were not so we should be faced with the absurd possibility that the walls of a closed vessel full of water would collapse under

the pressure that could be created by simply boring a tiny hole in one side - and the smaller the hole the greater the chances of collapse.

It is true that if one pumped pressure into such a vessel, the surface tension of the liquid in the capillary hole would be capable of holding that pressure without the liquid blowing out of the hole. Or the vessel could be connected to a negative pressure without the air leaking into the vessel through the hole. The pressure, positive or negative of course, will be determined by $2T/r$, where r in this case is the radius of the hole.

Now let us consider the hole itself. The edge of the hole is being hard put to maintain the concave shape of the meniscus, and if its walls were elastic, it would become wider, until the concave meniscus assumed the shape of plane water, according to the well known principle that potential energy must tend to be minimum.

In the case of a cellular structure - an assemblage of particles of various dimensions - it is not difficult to conceive that concave surfaces created by the absorption of moisture would tend to push the particles apart and widen the capillaries. This is not a case of volume-for-volume expansion, but rather one in which a portion of the structure is pushed apart at isolated points, leading perhaps to a reorientation of the pore space. In this region, therefore, we cannot expect a change in volume equal to the volume of water absorbed, which is the case when water is absorbed in bulk in macro capillaries. If we are taking into account bulk change in a porous body, the increase in apparent volume may actually be more than the volume of water absorbed.

Twelve soils were selected for this study. In every case the air-dry soils had been passed through a 1-mm mesh. Each soil was first made into a paste, and worked into the shape of a sphere of approximately the same size. These spheres were air-dried first and then placed over concentrated sulphuric acid in a vacuum desiccator. They were weighed occasionally until there was no change in weight over a period of two days. This was taken as the dry weight and volume of the spheres when free from water.

The dry spheres were then allowed to take up moisture from various humidities by keeping them over H_2SO_4 - water mixtures of appropriate humidity, starting with the lowest and gradually working up to the highest. The moisture content at every stage was determined by weighing, and the volume was found by the volumeter described. These spheres were then gradually dried stepwise, at different humidities, and volume determined at every equilibrium point. The results are given in Tables 102 and 103. The hysteresis effect is very well brought out in these results.

It will be seen that change in volume is considerable even on the absorption of moisture from humidities as low as 10%. There is no regularity in the results; the soils do not show the same change in volume per unit absorption of moisture. All the same, when the

percentage moisture absorbed is plotted against the values for percentage change in volume we get a mean line which shows in a general way the correlation between moisture absorbed and change in volume in this region.

TABLE 102. Volume changes in soils on moisture absorption at various humidities.

Soil No. P.C.	Relative humidity					
	10.4%	30.0%	50%	70.8%	90.9%	98.7%
5	(a) 0.14	0.85	0.86	0.86	0.96	1.10
	(b) 0.61	1.71	1.83	2.07	2.32	2.32
13	(a) 0.70	3.82	4.74	5.97	6.93	9.42
	(b) 1.2	1.8	3.8	5.8	7.8	8.2
107	(a) 0.701	1.28	1.31	1.35	1.39	1.43
	(b) 0.98	2.78	3.43	3.92	5.06	5.39
120	(a) 0.139	0.139	0.218	0.615	1.07	1.68
	(b) 0.58	1.16	1.05	1.74	2.43	3.37
121	(a) 0.39	1.37	1.62	2.05	2.46	2.48
	(b) 0.52	1.46	2.25	2.64	3.51	3.77
123	(a) 0.80	1.96	2.78	4.27	5.29	6.58
	(b) 0.90	2.10	3.30	4.65	6.0	8.70
132	(a) 0.53	1.23	1.54	2.06	2.40	2.87
	(b) 1.13	2.26	2.54	3.81	4.24	5.37
144	(a) 0.12	0.289	0.434	0.707	0.892	1.15
	(b) 1.07	1.76	1.88	2.01	2.27	2.97
175	(a) 0.35	1.32	1.47	1.76	1.97	2.42
	(b) 0.97	1.80	2.22	2.91	3.19	3.60
180	(a) 0.78	1.75	2.13	2.78	3.08	3.74
	(b) 0.89	1.53	2.30	2.80	3.30	4.32
201	(a) 0.26	0.85	1.18	2.08	4.02	5.40
	(b) 0.88	1.76	2.50	2.78	3.06	3.42
236	(a) 0.22	0.65	0.85	1.10	1.24	1.61
	(b) 0.39	1.44	1.56	2.08	2.34	3.12

a = Percentage moisture
b = Percentage change in volume

It must be emphasized that it is not expected that a certain change of moisture will always produce the same change in volume at all humidities or with all soils. As a matter of fact, the change in volume, if brought about by the surface tension residing at the film boundaries, will depend on the random grouping of the particles and

the interstitial spaces, and thus cannot show any regularity with respect to other soils. This must be typical of a random grouping of particles of all sizes.

TABLE 103. Volume changes in soils on moisture loss at various humidities.

Soil No. P.C.	Relative humidity				
	10.4%	30%	50%	70.8%	90.9%
5	(a) 0.30 (b) 1.22	0.89 2.06	0.92 2.18	0.99 2.24	1.13 2.36
13	(a) 2.93 (b) 1.60	4.72 3.0	5.49 5.0	6.22 6.8	7.52 8.05
107	(a) 1.5 (b) 3.09	1.31 3.58	1.34 4.07	1.36 4.4	1.43 5.21
120	(a) 0.59 (b) 1.72	0.61 2.05	0.63 2.16	1.01 2.60	1.3 2.93
121	(a) 1.31 (b) 1.55	1.71 1.93	1.83 2.70	2.38 3.09	2.73 3.6
123	(a) 3.1 (b) 2.55	3.05 3.75	3.68 4.95	4.58 5.40	6.32 7.80
132	(a) 1.78 (b) 2.25	1.60 3.09	1.70 4.07	2.41 4.35	2.56 5.19
144	(a) 0.17 (b) 1.48	0.46 1.82	0.57 1.93	0.74 2.13	0.97 2.39
175	(a) 0.68 (b) 2.09	1.50 2.65	1.55 2.93	1.80 3.35	2.25 3.49
180	(a) 2.04 (b) 1.27	2.11 1.90	2.42 2.54	3.17 3.04	3.50 3.81
201	(a) 0.76 (b) 2.48	1.18 2.76	1.49 2.90	2.40 3.04	5.65 3.37
236	(a) 0.55 (b) 1.56	0.80 1.82	1.00 1.95	1.32 2.47	1.39 2.73

(a) = Percentage moisture
(b) = Percentage change in volume

Volume Changes of Wood with Moisture Absorption

A somewhat better correlation and more regular increase in volume for unit increment of moisture would be expected from a substance like wood. This is actually so, as will be seen from the results given in Table 104. Several types of wood were examined. These were shaped into spheres and dried over sulphuric acid in the first instance. The technique of following volume changes was

exactly the same as in the case of soils. It is interesting to note that better grades of woods show less change in volume than poor quality woods. This is as it should be, as the main defect in poor quality woods is their tendency to warp in humid atmospheres. These volume changes at various humidities might give useful indications as to the quality of wood.

Volume Changes in Cement on Moisture Absorption

Spheres of convenient size were made with neat cement and allowed to set for 7 days in wet sand. They were then oven-dried at 80°C and kept over concentrated H_2SO_4 till thoroughly dry. They were then brought to equilibrium at various humidities and percentage

TABLE 104. Volume changes of wood at different humidities.

Wood	Relative humidity					
	10.4%	30%	50%	70%	90.9%	98.7%
Sagwan	(a) 0.25	2.3	3.2	5.4	8.6	12.6
	(b) 0.54	2.8	3.75	6.05	8.99	13.5
Cheel	(a) 0.26	2.6	3.90	5.10	7.60	12.20
	(b) 0.56	3.24	4.55	5.69	8.37	12.70
Shisham	(a) 0.08	2.40	3.40	4.72	7.20	14.0
	(b) 0.21	2.80	3.91	5.01	7.56	14.82
Deodar	(a) 0.45	2.00	4.20	5.90	9.10	13.2
	(b) 1.05	2.39	5.56	6.44	10.02	14.6
Padtal	(a) 1.80	3.60	4.03	5.80	8.42	14.3
	(b) 2.30	4.08	4.44	6.37	9.24	15.0
Kail	(a) 1.15	2.88	3.70	4.50	8.20	11.9
	(b) 1.72	3.56	4.52	5.30	9.18	12.5

(a) = Percentage moisture
(b) = Percentage change in volume

moisture absorption and volume change determined. The results are given in Table 105. Changes in volume with humidity are much more consistent for cement than for soils, showing that the grouping of particles in the former is much more regular.

Leaving aside individual differences, it is clear from the results presented in the foregoing that the regularity of volume changes in such diverse bodies as soils, wood and cement can only be reconciled with the capillary condensation theory of moisture absorption. No other hypothesis based on chemical action or on surface and residual valencies could fit the facts so well as the simple concept of condensation of moisture in micro capillaries.

Effect of Moisture Absorption on Soil Cohesion

Cohesion is the resistance offered by the soil to any force tending to break it. Measurement of cohesion and the influence of various factors such as size distribution of particles has been discussed

elsewhere. It is well to remember that cohesion in soils rests mainly on points of contact between particles; these can be decreased by the addition of coarser materials. Absorbed moisture could either lie as a monomolecular film on the exposed surface, in which case no change in cohesion will be expected, or it could enter the micropores, pushing the particles apart and decreasing the points of contact, in which case there will be a substantial decrease in cohesion.

The effect of moisture on soil cohesion has been studied chiefly in the wetter regions, where it is entirely accounted for by the surface tension of the liquid films which draw the particles closer together. The regions of hygroscopic moisture have remained practically unexplored, partly on account of the difficulty of accurate measurements, and partly because in this region the soil is supposed to have reached a state of maximum packing which is not disturbed by the loss or gain of moisture.

TABLE 105. Volume changes in cement on moisture absorption.

Humidity (%)	Moisture absorbed (%)	Change in volume (%)
10.4	0.11	0.18
30.0	0.38	0.60
50.0	1.25	2.13
70.8	2.46	3.26
90.7	3.62	4.40
98.7	6.28	6.87

If moisture absorption at lower humidities was purely a phenomenon taking place on the exposed surface in mono- or multimolecular layers, we should expect no change in cohesion due to moisture absorption in this region. If, on the other hand, the interstitial spaces were being filled and the particles pushed apart, resulting in an increase in volume as is actually the case, then there should be a substantial decrease in cohesion on moisture absorption.

The experimental evidence in support of this hypothesis was obtained by studying the cohesion of single-base soils. These were prepared by first removing all the exchangeable bases by 0.05N HCl treatment and then adding hydroxides of various metals. The soils were dried over H_2SO_4 and then allowed to take up moisture at various humidities obtained by confining H_2SO_4-water mixtures in vacuum desiccators. The equilibrium condition regarding moisture absorption was obtained in 6 to 7 days (Fig. 55A).

The enormous decrease in cohesion within a range represented by as low as 1% moisture content can be accounted for satisfactorily only on the basis of capillary condensation. The general similarity of the various curves and their close resemblance indicates that the same cause must be operative in all cases, namely, a decrease in the points of contact brought about by the absorption of moisture even at a humidity as low as 10%.

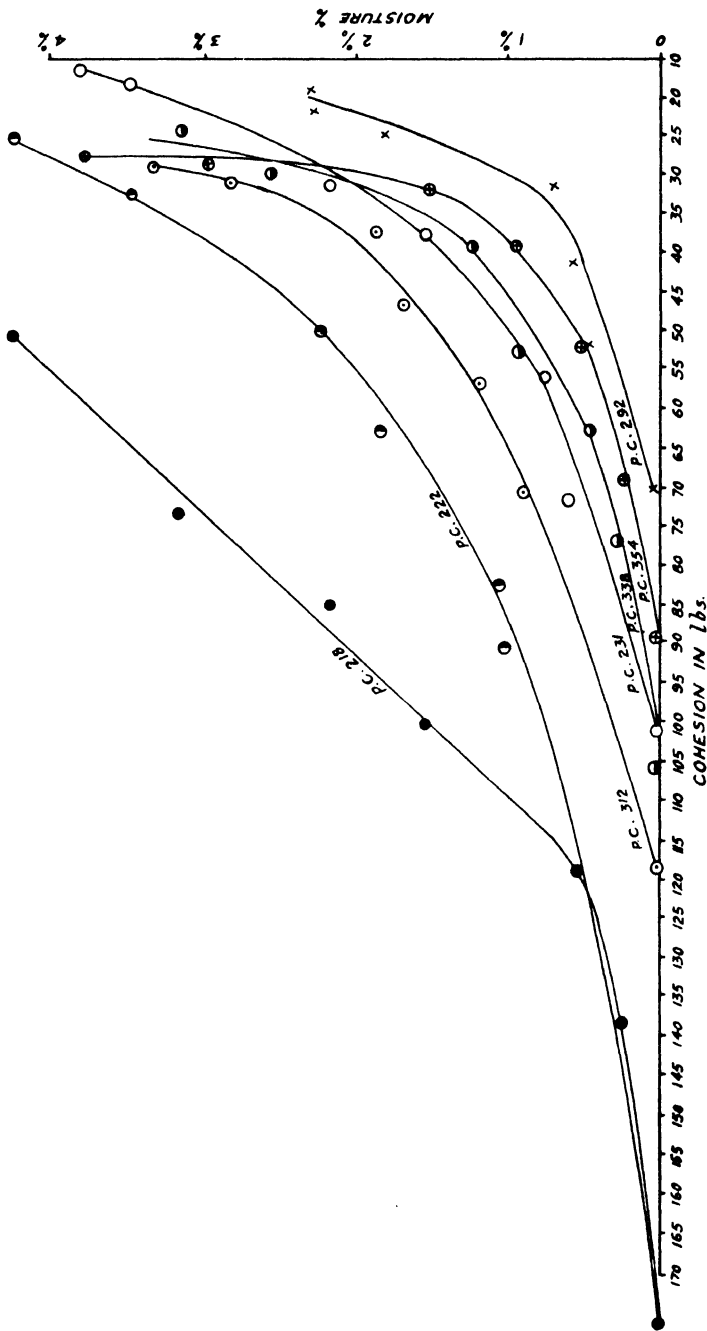



Fig. 55a. Relation Between Moisture Content and Cohesion of Soils

It will be noticed that the first lot of moisture produces the greatest effect. This is easily comprehensible, as the strongest bond must exist between particles of the smallest size, and it is the micropores between these particles that will absorb moisture first from the lowest humidity; therefore, the decrease in cohesion is comparatively greater. This is shown in a more striking manner in Fig. 56, in which the cohesion values are plotted against the humidities with which the soils are in equilibrium.

Fig. 56. Cohesion of Soils at Different Humidities

If the percentage decrease in cohesion is plotted against the percentage increase in moisture, practically all the points fall on one smooth curve (Fig. 57). From this the relation between moisture and percentage reduction in cohesion can be worked out.

Effect of Alternate Drying and Wetting on Soil Cohesion

We have seen that the increase in volume of the soil on moisture absorption is caused by a shifting of the particles, which causes a weakening of the cohesive bonds. On redrying the soil, the particles can be expected to return only partially to their original position, especially on account of the hysteresis effect. These changes in volume caused by alternate drying and wetting, if repeated several times, would ultimately result in a permanent weakening of the

cohesive bonds between soil particles. This conclusion is perfectly logical if we accept the capillary condensation theory of soil moisture.

Two soils (P.C. 218 and P.C. 354) were examined in this connection. The wetting and drying were carried out by keeping them alternately at the following pairs of humidities in desiccators over H_2SO_4 - water mixtures:

I. 0-10, 0-30, 0-50, 0-70, 0-90, 0-99%
II. 10-30, 10-50, 10-70, 10-90, 10-99%
III. 30-50, 30-70, 30-90, 30-99%
IV. 50-70, 50-90, 50-99%
V. 70-90, 70-99%
VI. 90-99%

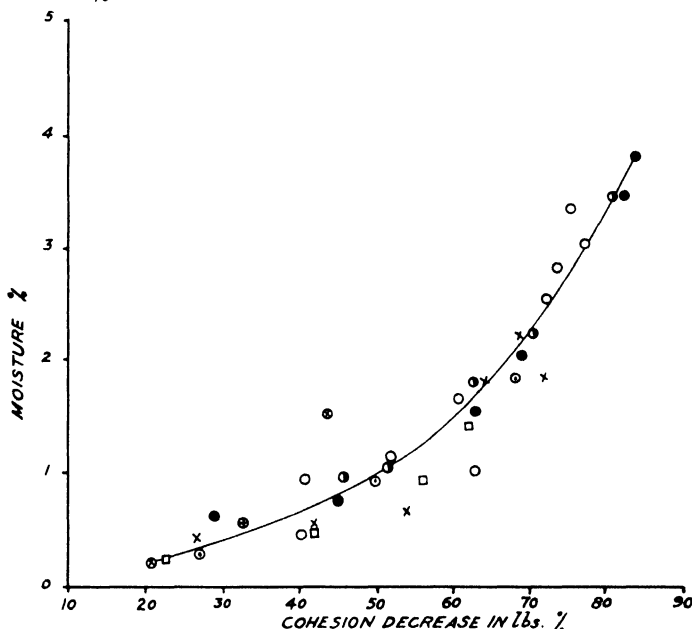



Fig. 57. Percentage Decrease in Cohesion of Soils for Different Moisture Contents

In the first instance the relation between moisture content and cohesion for each of the two soils was plotted on a fairly open scale. After each series of alternate wetting and drying, the moisture content of the pellets was determined and the cohesion value interpolated from these basic curves, which represented the relation as it existed without subjecting the soil to wetting-drying treatment. Any decrease in cohesion above this value was taken as the true effect of alternate drying and wetting. This procedure is necessary, as the additional moisture left in the soil on drying is likely to have its own effect in decreasing cohesion as a result of hysteresis; unless this is allowed for, the decrease might appear too great, whereas the actual value may not be very high.

The results are plotted in Fig. 58, which shows that in every case there is an appreciable decrease in cohesion, which becomes more and more pronounced as the number of alternate wettings and dryings increases. It is remarkable that even when the drying and wetting alternates between 0 and 10% humidity, there is appreciable change in cohesion, which is in fact of the same order of magnitude as at other humidities. As might be expected, the change in cohesion is slight when the humidity changes take place above 70%; for in this case only comparatively coarse particles are involved.

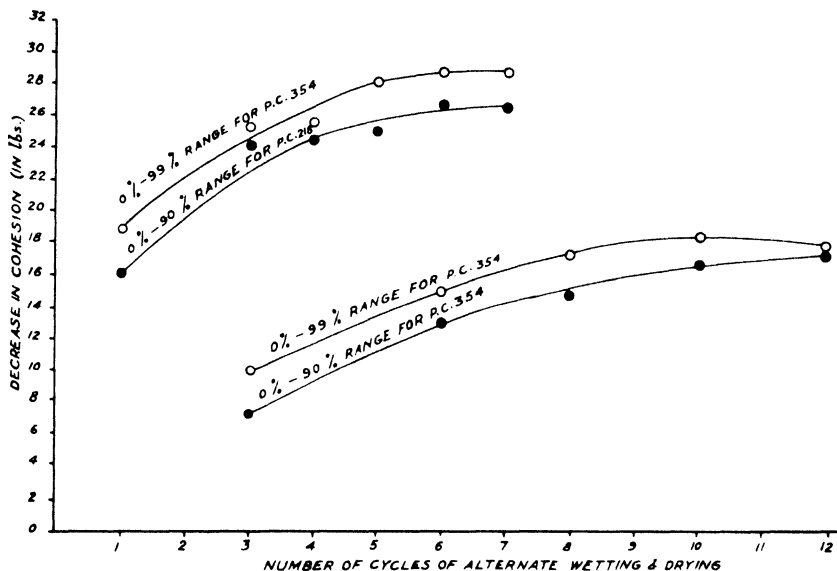



Fig. 58. Decrease in Cohesion of Soils after Different Cycles of Alternate Drying and Wetting

Effect of Alternate Drying and Wetting on the Cohesion of Soil Heated to Different Temperatures

When soil is heated to the fusion temperature the smallest particles melt and bind the larger ones together, creating a stable conglomerate that shows no signs of disintegration on contact with water. The cohesive forces induced in fused particles are apparently enough to overcome any disruptive forces brought about by the surface tension of absorbed water films.

However, since moisture is absorbed, alternate drying and wetting may still result in a slight change in the cohesion. Soil P.C. 354 was heated to different temperatures and subjected to alternate drying and wetting between a state of complete dryness and different humidities (Table 106). It will be seen that when the soil pellet has been heated to 900°C (the fusion temperature) there is practically no change in cohesion on alternate drying and wetting. It is evident that when the particles have been fused, they can withstand the internal strains due to surface tension without disintegrating.

It is to be noted that moisture absorption is considerably decreased when soil is heated to the fusion point, and even to 650°C. In both cases the decrease in cohesion due to alternate wetting and drying is inappreciable. In this respect ignited soil differs from cement in the sense that, whereas the former absorbs hardly any moisture, the latter can take up large quantities of moisture with a corresponding increase in volume.

TABLE 106. Effect of alternate drying and wetting on the cohesion of soil heated to various temperatures.

No. of alternates	% decrease of cohesion at humidity intervals			
	0 - 50%	0 - 70%	0 - 90%	0 - 99%
Heated to 230°C				
1	0.8	0.3	0.2	0.3
2	0.3	0.6	4.6	3.9
3	1.6	3.9	4.0	5.6
4	3.9	4.6	5.3	7.4
Moisture (%)	1.17	...	2.81	3.85
Heated to 400°C				
1	3.9	3.6	4.4	2.9
2	8.2	5.8	7.2	5.3
3	7.9	7.1	9.3	8.2
4	8.4	11.1	6.5	9.5
Moisture(%)	1.22	1.86	2.41	3.10
Heated to 650°C				
1	0.6	0.4	–2.0	–0.9
2	0.1	0.4	0.2	0.2
3	1.4	0.1	0.1	0.8
4	2.0	1.6	2.4	2.9
Moisture (%)	0.31	0.43	0.50	0.62
Heated to 900°C				
1	0	0.1	0.3	0.4
2	1.0	–1.2	0.1	1.1
3	0.2	0.3	0.1	1.4
4	1.2	1.1	0.6	1.2
Moisture (%)	0.15	0.16	0.28	0.42

It is interesting to note that burnt bricks have been known to last for centuries, whereas the life of cement is limited. These results bring out the importance of changes in atmospheric humidity on the weathering of rocks. Hitherto sufficient importance has not been attached to this factor. No doubt changes of temperature can also produce volume changes, and thus cause disintegration, but such changes will be confined to the superficial layer. It is also doubtful that a general increase in volume can have such a far-reaching effect as the internal stresses and strains induced in the micro capillaries, causing dislocation of the particles and breakdown of the cohesive forces.

CHAPTER XVI

MOISTURE ABSORPTION BY METALLIC OXIDES

It is well known that metallic oxides obtained from different sources and in different manners exist in different states of subdivisions. It is possible to measure the size distribution of their particles; this, together with their hygroscopic properties, should furnish additional evidence in favor of the capillary condensation theory of moisture absorption. The following oxides prepared in different ways were examined:

I. Copper Oxide
- (a) By heating copper oxalate.
- (b) By heating copper carbonate.
- (c) By heating copper nitrate.
- (d) Precipitating from copper citrate as hydroxide and subsequent heating.

II. Ferric Oxide
- (a) By heating ferric nitrate.
- (b) By heating ferrous ammonium sulphate.
- (c) By heating ferric carbonate
- (d) By precipitating from ferric chloride and subsequent heating.
- (e) By precipitating from ferric nitrate and subsequent heating.

III. Aluminum Oxide
- (a) By heating aluminum oxalate.
- (b) By heating aluminum nitrate.
- (c) By precipitating from aluminum nitrate.

Moisture absorption was studied in the usual way by placing samples over H_2SO_4 - water mixtures in desiccators. The mechanical analysis was determined by the pipette technique, assuming the application of Stokes' Law. For this purpose the density of the oxide was determined in every case. No preliminary treatment for

dispersion was given in one set of experiments, whereas sodium hydroxide was added for peptizing in the other. The results of mechanical analysis with and without dispersing agent are given in Table 107.

It will be seen that oxides of the same metal prepared in different ways show fairlv large variations in their size-distribution curves.

TABLE 107. Mechanical analysis of oxides of Cu, Fe, and Al, prepared by different methods.

Source		% of particles of different sizes						
		0.06	0.04	0.02	0.01	0.006	0.004	0.002
				Copper oxides				
Cu oxalate heating	A	16.2	16.2	7.5	3.0	2.7	1.5	0.25
	B	22.5	13.5	11.5	4.5	4.25	2.25	-
Cu carbonate heating	A	50.0	32.7	14.0	11.5	11.0	9.7	8.75
	B	64.5	32.0	24.0	14.0	8.5	5.0	
Cu nitrate heating	A	32.3	28.7	11.0	4.2	2.2	2.2	1.1
	B	33.0	30.5	17.0	6.5	4.0	2.5	
Cu nitrate precipitation	A	33.1	31.2	8.7	3.1	-	2.25	0.55
	B	-	-	-	-	-	-	-
				Iron oxides				
Fe carbonate heating	A	85.0	88.0	79.0	37.0	23.0	3.0	-
	B	86.0	85.0	80.0	45.0	22.0	-	4.0
Fe ammonium sulphate heating	A	99.0	68.5	13.0	8.0	6.0	3.5	-
	B	95.0	70.0	20.0	15.0	7.0	-	5.0
Fe nitrate heating	A	40.0	40.0	13.0	4.0	2.0	1.5	1.0
	B	42.5	42.0	12.5	5.0	2.5	-	1.0
Fe nitrate precipitation	A	31.6	20.3	17.0	1.7	-	2.3	2.0
	B	29.0	28.5	15.0	5.0	3.5	-	2.5
				Aluminum oxides				
Al oxalate heating	A	19.0	11.0	7.5	6.5	5.5	4.0	-
	B	20.0	12.0	6.0	5.5	3.0	-	1.5
Al nitrate heating	A	35.8	20.4	7.2	2.6	2.5	1.1	0.5
	B	29.5	24.0	10.7	4.0	1.0	-	1.0
Al nitrate precipitation	A	31.6	29.4	8.0	2.0	-	0.55	0.55
	B	27.5	25.2	11.5	7.5	6.5	-	1.0
Al sulphate precipitation	A	28.9	20.9	5.5	3.0	2.0	1.0	0.75
	B	-	-	-	-	-	-	-

A = without dispersing agent B = with NaOH as dispersing agent

In the case of copper oxide, for instance, it is seen that of the various samples the one obtained from copper carbonate on heating exists in the finest state of subdivision. The material obtained from copper oxalate, on the other hand, is found to be the coarsest of the oxides of copper.

From these observations it is difficult to say what actually determines the mechanical composition of an oxide. Whether it is the mode of preparation, the nature of the material from which it is obtained, the type of reaction involved, or the replacement of a par-

ticular group by another, which is primarily responsible for dividing and subdividing oxide particles and orienting them in a particular pattern of aggregate formation, is more than can be concluded from the data in hand. There is some indication that oxides obtained by calcining the carbonates are probably the finest. It is not unlikely that the temperature at which an oxide is roasted may have a lot to do with its texture. It is to be noted that CO_2 is driven off at a

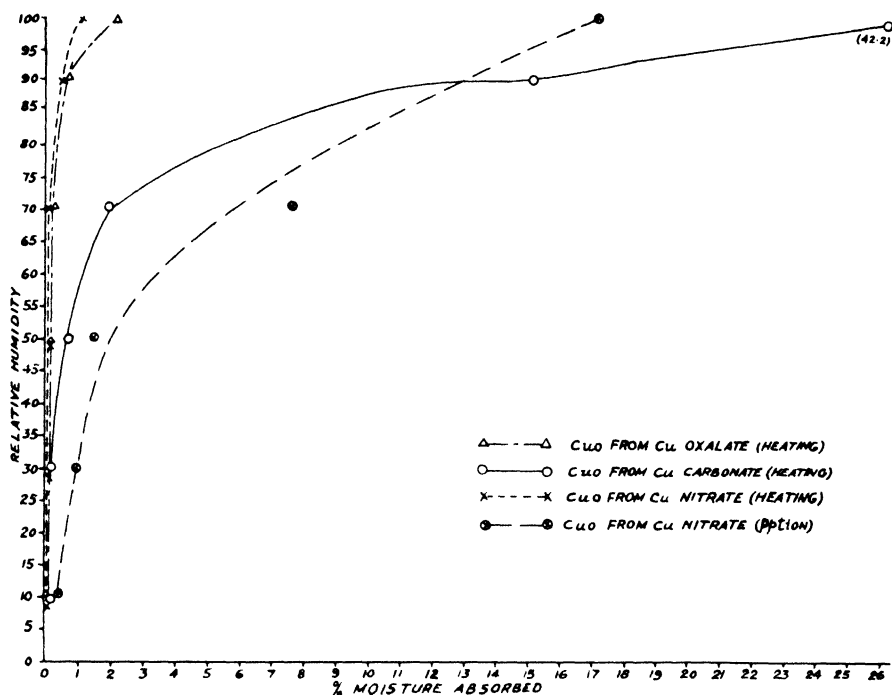



Fig. 59. Vapor Pressure Curves of CuO Prepared in Different Ways

comparatively low temperature, whereas in the formation of other oxides, the higher temperatures necessary may lead to a certain amount of fusion of the finest particles into aggregates.

Following the general principles of soil dispersion it might appear that these oxides will show greater dispersion when peptized with an alkali. It is not surprising, however, that alkali causes peptization to a limited extent only, and that order of the fineness of the various samples does not undergo any noticeable change. We must remember that soils are acidoids, whereas these oxides are basoids. The results of moisture absorption by the different oxides at various humidities are plotted in Figs. 59, 60 and 61.

The variations in the hygroscopicity of a particular oxide when obtained by different methods are appreciable. In the case of copper oxide, for instance, it is seen that of the various samples the one

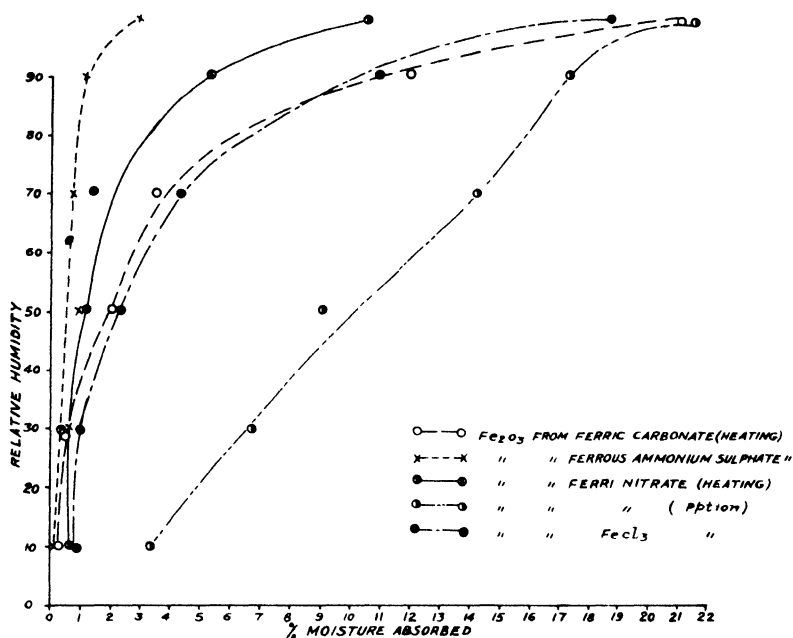



Fig. 60. Vapor Pressure Curves of Fe_2O_3 Prepared in Different Ways

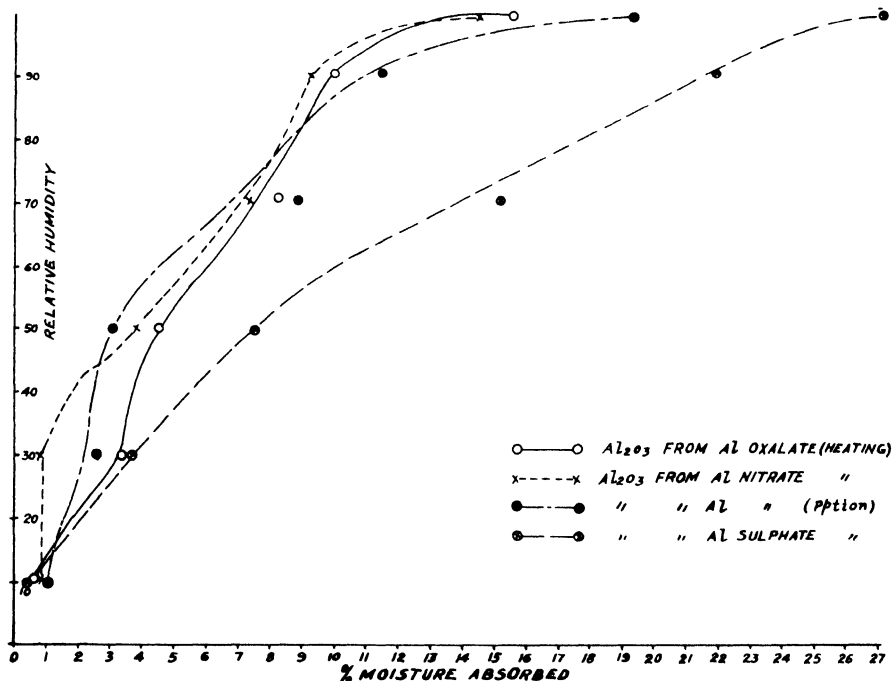



Fig. 61. Vapor Pressure Curves of Alumina Prepared in Different Ways

obtained from $CuCO_3$ on heating is hygroscopic to the largest extent. This is consistent with its finest mechanical composition (Table 107). The oxalate and the nitrate yield oxides which are poor in hygroscopic properties, while the one obtained from the nitrate by the precipitation process is fairly hygroscopic, and at lower humidities compares favorably even with that obtained from carbonate. From these results it is quite apparent that, unlike soils, there is no correlation between the size distribution of particles and vapor-pressure curves. This is not surprising in view of the fact that it may not be possible to overcome the cohesive forces between the compound particles in every porous body.

As a matter of fact, it is only in the case of soils that complete disintegration of the aggregates into primary units is possible. There are many substances which admittedly have a cellular structure and in all probability are composed of particles of various sizes with interstitial spaces between them; however, there is no means of breaking up the aggregates into primary units. A notable example is absorbent carbon, which cannot be dispersed in any liquid and yet gives a well defined vapor-pressure curve and thus must have a specific size distribution of capillaries and probably of particles too.

There is one very important point about soils which is unique in the domain of capillary systems. All natural soils give smooth summation curves and consequently smooth vapor-pressure curves. This is characteristic of the natural weathering forces which brought about the gradual disintegration of the parent rock and converted it into soil in the course of time. The process can be visualized as the gradual breakdown of the larger particles into smaller and smaller units. This has proceeded smoothly and regularly, though slowly, throughout the centuries. Most of the capillary systems in the organic world are built-up structures which are so much influenced by rapidly changing environments that any regularity in their physical make-up would hardly be expected.

Such is also the case with the oxides under discussion; they do not give smooth size-distribution curves nor can they be expected to give smooth vapor-pressure curves. A slight alteration in the temperature or rate of reaction may have a profound influence on the size distribution and geometry of the space lattice of primary particles as well as aggregates.

It is one of the strongest arguments in favor of the capillary condensation theory that a smooth vapor-pressure curve is associated only with a smooth size-distribution curve. The vapor-pressure curves of soils have only one point of inflection, whereas other capillary systems, like natural organic bodies or oxides, may show more than one. The existence of more than one inflection point, or even lack of smoothness, is inconsistent with any chemical view of adsorption of water vapors; for such a view must take note only of the extent of the surface, and once the surface is there to adsorb

moisture in monomolecular or multimolecular layers, there is no reason why one should not expect a perfectly smooth adsorption-isotherm or vapor-pressure curve. The moment we bring in the nature of the surface we move away from the chemical view.

The preparation of copper oxide from copper carbonate involves the elimination of a molecule of CO_2, whereas its preparation from oxalate and nitrate involves the elimination of CO_2 plus CO and NO_3 plus NO_2, thus leaving the product more porous, with capillary spaces of larger dimensions. Such oxides, therefore, may not absorb any moisture from low humidities, which is actually the case.

The precipitated copper oxide is obtained in a gelatinous form by the replacement of an NO_3 group taking place in solution; no elimination of a molecular species *in situ* is involved, unless it is the liberation of water molecules during subsequent dehydration of the precipitate. But the elimination of a water molecule will leave pore spaces of smaller dimensions than in the case of CO_2. The material obtained by this process, therefore, is more hygroscopic than any other sample at lower humidities. At humidities higher than 90% the oxide obtained from $CuCO_3$ is more hygroscopic than this sample. This is to be expected from the larger capillary sizes which the former is likely to have on account of the elimination of CO_2 in its preparation.

It appears also that when two or more gases are simultaneously eliminated, i.e., when the size of the radical to be eliminated is large, the resulting product may contain capillary spaces which are too large to absorb any moisture even from fully saturated atmospheres (compare moisture absorption results of copper oxide obtained from oxalate and nitrate).

The results obtained in the case of ferric oxides can be explained on the same basis. It is interesting to find that the material obtained from ferric carbonate on heating has the highest hygroscopicity. The comparison of moisture absorption properties of the oxide obtained from ferric carbonate and nitrate as well as ferrous ammonium sulphate emphasizes the effect of the size of the eliminated radical on the hygroscopicity of the residual material. Ferrous ammonium sulphate, as expected from these considerations, gives the least hygroscopic, and ferric carbonate the most hygroscopic oxide. The two samples of ferric oxide obtained by precipitation reactions (from ferric chloride and nitrate) are seen to be more hygroscopic than the one obtained by heating the carbonate, at lower humidities; the difference decreases with increasing humidities and almost disappears at higher humidities. This is quite in accord with similar observations made on copper oxide. In the precipitation process too, the nature of the replaced group has some influence on the hygroscopic properties of the resulting material, as the samples obtained from ferric nitrate and ferric chloride show appreciable differences in their moisture absorption values at lower humidities.

Similar conclusions can be drawn from the results on alumina samples. The materials obtained by heating the nitrate and oxalate have lower moisture absorption values than those obtained from nitrate and sulphate by precipitation reactions. The oxide precipitated from sulphate is more hygroscopic than that from nitrate. The samples obtained from oxalate and nitrate, on heating, differ much from one another in their size-distribution curves but resemble each other closely in their hygroscopicities.

The absence of parallelism between hygroscopicity and mechanical composition of various oxides when prepared in different ways indicates that in these materials the size distribution of capillary spaces is not related to the size distribution of particles, either because the particles are not in the form of close or open packing, but are distributed at random, or our method of dispersion fails to reveal a true picture of the size distribution. This is not surprising, since the total capillary space and size distribution of an oxide are factors which are very probably governed by the mode of its preparation, the type of reaction involved, and the nature and size of radical eliminated.

Of the various metallic oxides alumina occupies a unique position. When precipitated as hydroxide it comes down in the form of a gelatinous mass, which is known to be a good absorbent. Hitherto the procedure followed in the preparation of the oxides has been a more or less general one. Either the compound was roasted until the oxide was left behind, or the hydroxide was heated until it was converted into the oxide. As pointed out before, in all these absorbents the technique of preparation has a profound influence on the absorptive properties of the resulting compound. The very low hygroscopicity of the oxides at low humidities appeared to be due to the coalescence of the finest particles by heat, and consequently the removal of the finest capillaries, which are responsible for moisture absorption at low humidities.

The following oxides of aluminum were prepared according to standard methods, particularly bearing in mind the precaution that wet alumina should not be dried rapidly at a higher temperature. The cellular structure of this material is best maintained when the drying is slow and at a comparatively low temperature (50 to 60°C).

From Aluminum Amalgam

Alumina from aluminum amalgam was prepared in the manner described by Adkins. Briefly, the method consists in treating the amalgam with water. The amalgam was prepared by covering fine strips of pure aluminum cut from thin sheets with 0.5% solution of mercuric chloride for 1 1/2 minutes and subsequent washing. After the completion of reaction between the amalgam and water, the precipitated alumina was collected on a filter paper, and washed and dried at 60 to 70°C, as recommended by Chowdhry and Bagchi.

From Aluminum Nitrate

The aluminum nitrate was calcined on an ordinary burner, with frequent stirring. The heat was so regulated that the temperature was not allowed to go any higher than that necessary for the evolution of nitrous fumes. The resulting pure white solid passed a 200-mesh sieve with a little grinding and gave no test for nitrate.

By Precipitation from $AlCl_3$, $Al_2(SO_4)_3$: Potash Alum and Soda Alum

Aluminum hydroxide was obtained in every case as a flocculant, gelatinous precipitate by the slow addition of ammonia with vigorous stirring to the aluminum salt solution, keeping the temperature below 24°C. Chowdhry and others have reported that higher temperature yields comparatively poor adsorbents. The precipitate in every case was washed free from impurities and dried at 60 to 70°C in an air oven.

The various samples of alumina were then activated at 200°C in a stream of carbon dioxide for two hours. The results of moisture absorption by various samples at different humidities are given in Table 108. The samples of alumina prepared by precipitating from

TABLE 108. Moisture absorption by alumina prepared in different ways at various humidities.

Alumina prepared	% moisture absorbed at different humidities					
	10%	50%	70%	90%	95%	99%
Al amalgam	0.8	3.2	4.5	4.5	6.9	7.08
$Al_2(SO_4)_3$	7.1	14.05	16.1	23.9	53.5	62.0
$Al(NO_3)_3$	3.17	7.7	12.0	19.4	28.8	40.4
$AlCl_3$	11.1	12.5	15.6	21.6	48.0	57.3
Soda alum	6.9	7.5	11.1	12.3	19.1	19.1
Potash alum	6.2	6.2	10.7	12.0	15.8	18.9
Soil P.C. 13	4.81	9.33	11.78		16.8	19.57

Al_2Cl_3 and $Al_2(SO_4)_3$ absorb moisture to nearly the same extent. The alumina prepared by calcining $Al(NO_3)_3$ absorbs much less moisture from atmospheres of lower humidities; at higher humidities the moisture absorption increases, though it still does not equal the amount absorbed by the other two samples. This shows that most of the capillaries in this sample are of comparatively large size. This is probably due to the elimination of NO_2 gas during the calcination of $Al(NO_3)_3$; continuous elimination of NO_2 and O_2 would leave larger spaces between the molecules of alumina.

The samples prepared by precipitation from soda and potash alums absorb almost as much moisture as the one prepared from $Al_2(SO_4)_3$ at 10% humidity; but with higher humidity the difference in their moisture-absorption capacity continues to increase, the amount absorbed by the latter sample becoming ultimately far in excess of the others. This is because the elimination of K_2SO_4 plus Na_2SO_4 from potash and soda alums leaves much larger pore spaces

which cannot effectively absorb moisture from the vapor phase. It is also worth noting that these two samples prepared from alum resemble each other in absorbing the same amount of moisture at all humidities. The sample prepared from aluminum amalgam absorbs very little moisture, even from fully saturated atmosphere.

These results very clearly show that in preparing activated alumina, the method of preparation and composition of the starting material is of great importance. In the above case we have each time chemically identical material, namely Al_2O_3, yet it possesses remarkably different moisture-absorption capacity when prepared from different sources. This also shows incidentally that the total pore space in an activated material is not the only consideration. In fact, the size of the capillaries is a much more important factor. The alumina prepared, for instance, from potash alum or by heating $Al(NO_3)_3$ will have larger capillary spaces because of the elimination of the larger molecules, but at the same time the capillaries will be too big for effective moisture absorption from the vapor phase.

The moisture absorption results for a soil sample (P.C.13) at different humidities are also included in Table 108. The similarity between soil and alumina is very striking. Unlike the oxides prepared at random, the vapor-pressure curves in this case are smooth and regular, and show only one point of inflection. The most important part of the procedure in preparing these oxides was vigorous stirring during precipitation and slow drying of the resulting material. Unless this precaution is taken, grouping of the aggregates takes place at random without any order. The lack of uniformity in one case and the perfect regularity of the vapor-pressure curve in the other are further evidence of the applicability of the theory of capillary condensation.

Other theories are primarily concerned with the extent of the surface and perhaps to a limited degree with its chemical nature, which is the same in all cases for a single substance. On the basis of the capillary condensation theory, moisture absorption is merely a reflection of the size distribution of microcapillaries. The vapor-pressure curve, therefore, may take any shape. It may show one point of inflection, but it would not be surprising if it had two or even more; on the basis of any other theory, however, this would be a considerable strain on the imagination, for the only course left would be to postulate a size distribution of "active points" on the surface of the adsorbent.

CHAPTER XVII

MOISTURE ABSORPTION BY SILICA AND SILICATES

In comparatively recent years considerable literature has sprung up on the methods of preparation and utilization of activated silica as an absorbent for water and other vapors. Among the earliest methods of preparing activated silica is that of Patrick. The method in brief consists in mixing hot sodium silicate solution of 1.185 specific gravity with an equal volume of 10% solution of HCl. After the gel is set it is broken into pieces and the salt and excess acid washed out with water. It is then air-dried and finally activated at 300°C.

Holmes and Anderson showed that the porosity of the gel depends upon the extent of drying before washing and on the rate of drying. These workers also prepared a porous silica gel by adding ferric chloride (instead of HCl) to sodium silicate solution, drying the gel so obtained to a moisture content of 55 to 60%, and then removing the iron oxide from the firm solid by treating with acid. In the same way Holmes prepared other silica gels by coprecipitation with other oxides, such as alumina, calcium oxide, chromic oxide, copper oxide and nickel oxide. On washing away these oxides, although the same chemical compound (SiO_2) was obtained in each case, the sample had varied adsorption capacity for different gases and vapors.

Holmes showed that variations in the rate of drying have a decided influence on the quality of the product, the slower rate giving the better product. Holmes and Elder found that increase in temperature of the acid treatment of the gel (in order to wash away the metallic oxides) from 30 to 100°C increased the porosity of the gel.

Silica and silicates occupy a unique position among natural and artificial absorbents in the inorganic world. There are almost infinite variations in their absorbing properties due to the method of preparation, even a slight change in the technique producing a profound change in the absorption. The only explanation of this fact is that the vapor absorption is due to capillary condensation, as the size distribution of capillaries would admit of infinite variations. Moisture absorption by silica and silicates prepared in a variety of ways thus offers a fruitful line of investigation in elucidating the mechanism of moisture absorption by capillary systems in general.

Moisture Absorption by Activated Silica Samples Prepared by Different Methods

General methods for the preparation of silica have been suggested from time to time and superiority is claimed for each by individual workers. Some of the chief methods available are due to Patrick, Holmes, and Bartel and Fue. Silica gels have also been obtained for a long time from ammonium salts. The method consists in adding ammonium salt solution NH_4Cl, $(NH_4)_2SO_4$, etc., to equivalent solutions of Na_2SiO_3. Since weak acids, like silicic acid, are loosely combined with ammonia, as soon as an ammonium salt is added to sodium silicate solution gelatinous ammonium silicate is precipitated, from which the ammonia is easily washed out with dilute acid. The actual methods used in the preparation of these materials are outlined below.

Patrick's method. Patrick's silica is obtained by mixing with continuous stirring hot solution (50°C) of HCl containing 10% by weight of the gas with an equal volume of sodium silicate of density 1.185. The mixture sets to a gel in about an hour. It is then broken into small lumps, washed free from salts, etc., and then allowed to dry slowly at room temperature. The dried lumps are ground to pass 200 mesh, and then activated.

Holmes' method. Five samples of silica were obtained by this method. They were prepared from mixtures of different metallic oxides, silica gel being precipitated in the first instance by the addition of different salt solutions to solutions of sodium silicate. Ferric oxide-silica gel mixture, for instance, is formed by slow addition with violent stirring of 2 liters of 2N $FeCl_3$ solution to 625 cc of sodium silicate solution (sp. gr. 1.375) which has previously been diluted with 12.5 liters of water. The mixture is allowed to stand for 60 hours and then filtered through fine muslin; the gelatinous mass is allowed to stand in a layer about 5 cm deep for a few days till it can be handled and is then broken into uniform lumps about 2 cm in diameter. When the water content of the lumps falls to about 50 to 60%, which requires nearly a fortnight, the whole mass is kept in a bottle to prevent evaporation and allowed to "sweat" for a week. The mass, consisting of the hydrous oxide of both iron and silica, is then subjected to steam for one hour and heated to 80°C with 9N H_2SO_4, a process which dissolves the iron oxide. Repeated washings are then given to remove the iron and excess acid after which the gel is dried at approximately 150°C for 8 hours. It is then reduced to 200 mesh and activated.

In a similar way gels containing oxides of chromium, copper, cobalt and nickel mixed with silica are prepared by adding 5 cc of 0.22N solutions of the metallic chlorides to 50 cc of water glass solution (sp. gr. 1.375) diluted to one liter. The gels are then dried, steamed, treated with acid, washed, dried, and activated as described above.

Bartel and Fue's methods. A high grade of water glass is diluted to a specific gravity of 1.025 and neutralized with 1:1 HCl. Before the mixture has set to a gel, saturated nickel nitrate solution is added in the proportion of 200 cc of nickel nitrate to 1000 cc of silicic acid solution. The mixture very soon sets to a solid green gel and is allowed to syrenize at 90°C until the gel appears to be thoroughly dried. It is then washed with dilute HCl, until the filtrate no longer gives tests for Ni with dimethyl glyoxime. It is then heated at 250°C in a beaker for two hours and poured immediately into cold distilled water. This last treatment, which is repeated several times, causes larger granules to split apart and helps to remove the remaining traces of HCl. The gel is finally dried at 200°C, powdered to 200 mesh and activated.

Silica precipitated by the addition of ammonium salts. One pound of sodium silicate solution of specific gravity 1.2 is diluted with an equal volume of water, and to this 0.8735 equivalent of the ammonium salt dissolved in 3 liters of water is added. The resulting gel is broken into small lumps of 2" size after it has set for 24 hours, and washed with hot water to remove ammonium salts. Seven samples of silica were obtained by this method using NH_4Cl, $(NH_4)SO_4$, NH_4NO_3, $(NH_4)_2CO_3$, $(NH_4)_2CO_4$, ammonium tartrate and ammonium chromate.

Silica from fused sodium silicate. 20 grams of fused sodium silicate was boiled with 450 cc of 8N H_2SO_4 for two hours; after washing, the precipitated silica was dried at 150°C and then activated.

Activation of Silica Samples

The usual method of activating silica consists in passing air continuously over the sample heated to 200°C for about two hours; it can also be activated by passing CO_2 instead of air. A comparison of the moisture absorption capacity of the samples activated by the two methods showed that CO_2-activated samples absorb more moisture than air-activated ones at all humidities. It appears that passage of CO_2 over heated silica is more effective than air in removing the last traces of water during the process of activation. This is probably because the CO_2 passed was drier than the air. It is not possible to say exactly what the mechanism of activation is, but it appears very probable that it must be associated with the removal of the residual moisture, thus rendering the sample "drier" and so capable of absorbing more.

On perusal of the literature it is found that usually two hours of activation is recommended. During this time it is presumed that the maximum drying of the capillaries has taken place. The effect of the temperature at which activation is done has been studied in detail by Holmes and Eldu, who found that heating to a temperature anywhere between 100 and 800°C does not affect the quality of the sample. Heating beyond 800°C, however, was found to decrease activity appreciably. Usually, activation is performed at 200°C;

the author's experience, however, is that heating silica even to 450°C reduces its moisture absorption capacity considerably.

The effect of time of activation has not been studied in detail so far. It was therefore thought of interest to activate the samples for different lengths of time. Results of these experiments showed that the moisture absorption capacity of the sample at all humidities increases with the time of activation up to three hours. If activation is continued for a longer time, it seems that while little or no change is produced as far as moisture absorption from atmosphere

TABLE 109. Moisture absorption by various activated silica samples prepared in different ways.

Description of sample	% Moisture absorption at humidity					
	10%	50%	70%	90%	96%	99%
1. Patrick's gel	30.2	30.2	34.6	45.0	64.5	66.5
2. Holmes' gel with						
(a) $FeCl_3$	6.6	38.2	39.8	44.0	65.8	72.2
(b) Cr Chloride	6.3	28.4	28.4	62.6	62.6	67.4
(c) Co Chloride	5.9	35.8	38.0	63.6	64.4	70.4
(d) Ni Chloride	5.6	36.5	38.0	50.8	71.6	86.3
3. Bartel & Fue	20.8	26.0	27.2	48.8	74.0	90.0
4. From fused Na Silicate	12.0	13.9	15.5	21.7	38.1	38.1
5. Sodium silicate with						
Am. chloride	3.8	4.9	11.4	52.6	52.8	54.4
Am. sulphate	5.5	8.9	17.6	69.6	69.6	71.0
Am. nitrate	5.4	8.5	16.1	52.1	52.1	52.1
Am. carbonate	3.7	10.9	14.5	46.0	48.0	51.3
Am. oxalate	3.5	5.6	16.8	52.0	53.0	58.0
Am. tartarate	5.2	8.2	15.5	54.4	54.6	57.3
Am. chromate	1.0	3.6	18.5	40.2	40.2	43.0

of higher humidities is concerned, there is a fall in the values obtained from atmospheres of lower humidities (up to 50%).

It appears, therefore, that the period of activation should not exceed three hours. During this time most of the water present in the unactivated sample is removed. The rest of the water seems to be held much more firmly, apparently in such fine capillaries that when efforts are made to remove this water either by increasing the time of activation or by raising the temperature, the gel structure partially collapses, decreasing the moisture absorption capacity. In what follows, therefore, two hours' heating at 200°C in a stream of CO_2 was adopted as the standard activation procedure.

Results of moisture absorption by various activated silica samples prepared in different ways are given in Table 109.

These results give a clear concept of the comparative size of the capillary spaces of the various samples. At low humidities Patrick's silica gives maximum moisture absorption. The various types of Holmes' silica (as these are prepared from different metallic oxide-silica gels after dissolution of the metallic oxides) have wider capillaries and therefore absorb more moisture from atmospheres of higher humidities. At about 70% humidity the curves for these samples cross the curve for Patrick's silica gel, and at all humidities lower than 70%, the latter absorbs more moisture than do Holmes' samples. At higher humidities Holmes' silica is a better absorbent.

In this connection it may be mentioned that Holmes and his co-workers claim better adsorption capacity for their samples. This is because they determined absorption of benzene and other organic vapors from fully saturated atmospheres and concluded that their material was superior to Patrick's. The dissolution of metallic oxides from the coprecipitated silica gel prepared by Holmes' method no doubt leaves the resulting silica more porous, but it also results in wider capillaries, thus making the samples poor adsorbents of moisture and other vapors from atmospheres of lower vapor pressures.

Patrick's silica in fact is superior to that of Holmes if absorption is to take place from atmospheres of lower vapor pressures; the claim of Holmes, etc., that their sample is a better adsorbent is true only when adsorption is to take place from saturated or nearly saturated atmospheres. It is also clear that Patrick's silica as an efficient drying agent is superior to that of Holmes, but the latter is more effective if only partial drying is required.

Bartel and Fue's silica also compares favorably with Holmes' silica obtained from nickel oxide silica gel, which it resembles in the method of preparation, as it absorbs comparatively more moisture at all humidities higher than 90%.

The silica samples prepared by treating fused sodium silicate with H_2SO_4 is a poor adsorbent at all humidities except at 10%, at which humidity it compares favorably with some of the best absorbents. Evidently the method of preparing this silica precludes the formation of larger capillaries, but the subsequent treatment with H_2SO_4, which removes the sodium hydroxide, must leave behind a network of the finest capillaries, which are responsible for moisture absorption at lower humidities.

Obviously larger capillaries are also present, and there is a fair amount of moisture absorption between 70 and 96% humidity. A word about the method of preparation of this material: Water glass is dropped on a hot plate; the water quickly evaporates, leaving behind a spongy mass of dry silica. It appears very porous, but evidently the spongy consistency is due to very large pores which are unable to absorb any moisture from the vapor phase, just as all the pores in a sponge will not be filled by water even from an atmosphere fully saturated with vapors.

There is a general similarity in moisture absorption among the various forms of silica prepared by the addition of ammonium salt solutions to sodium silicate solution (Table 109). This is to be expected, since in each case the precipitation of silica involves the same chemical reaction.

It is usually recommended in the methods of preparing activated silica that the materials to be activated should be ground to some fine mesh, varying from 100 to 200. To see if the ground material absorbs moisture to a larger extent than the unground, two samples of silica were prepared by the addition of NH_4NO_3 and $(NH_4)_2SO_4$. In each case one portion of the sample was ground to pass 200 mesh

TABLE 110. Effect of grinding on the moisture - absorption properties of silica.

Silica prepared from	% Moisture absorption at humidity					
	10%	50%	70%	90%	96%	99%
1. Sod. silicate + Am. Sulphate						
Lumps	5.5	8.9	17.6	69.6	69.6	71.0
Powder	3.8	8.3	15.7	59.8	59.8	59.8
2. Sod. silicate + Am. Nitrate						
Lumps	10.0	13.2	23.4	61.7	61.7	61.7
Powder	5.4	8.5	16.1	52.1	52.1	52.1

and another portion was not ground at all, but was activated in the form of lumps, each lump being nearly 5 mm in diameter (Table 110).

Grinding, it appears, breaks down some of the finer capillary walls, thereby adversely affecting the vapor absorption property. These results would be difficult to explain on any other basis except the capillary condensation theory. It is inconceivable that any chemical action would be adversely affected by grinding, but a mechanical collapse of the capillaries or a reorientation of the relative distances resulting in a more compact mass may be expected on grinding.

As pointed out before, the absorptive properties of silica are greatly influenced by the manner in which it is prepared. In this connection the stage to which drying should be carried before washing the gel is especially important. Sufficient data, however, are not available in the literature to indicate why the drying should be pushed to a given extent. To throw light on this problem, silica was prepared according to the following methods:

(1) Patrick's method: By mixing equal amounts of sodium silicate solution of density 1.185 and 2.74N HCl.

(2) By mixing 0.3N solutions of
- (A) ammonium chloride
- (B) ammonium carbonate
- (C) ammonium acetate

with sodium silicate solution of density 1.085 in equal volumes.

(3) By mixing 980 cc of 1.92N ferric chloride solution with 8 liters of sodium silicate solution of density 1.030.

(4) By mixing 1750 cc of 0.44N aluminum sulphate solution with 3 1/2 liters of sodium silicate solution of density 1.030.

(5) By mixing 2400 cc of 0.44N chromium chloride solution with 4.8 liters of sodium silicate solution of density 1.030.

TABLE 111. Moisture absorption from various humidities by silica dried to different degrees.

Sample No.		Dried to moisture (%)	% Moisture at various humidities					
			10%	30%	50%	70%	90%	98%
I	a	Not dried	16.9	22.9	27.1	32.8	70.4	94.8
	b	80.5	12.4	16.6	19.4	34.3	59.9	80.9
	c	77.5	11.2	14.8	22.3	24.7	49.6	70.0
	d	56.3	8.0	12.6	21.9	22.5	38.6	62.6
	e	41.0	6.2	8.7	13.2	13.9	25.6	53.5
IIA	a	88.5	11.3	13.2	16.0	23.5	50.0	62.5
	b	70.0	15.6	29.2	30.0	33.7	66.9	80.9
	c	32.1	7.4	9.1	13.2	25.9	53.9	61.8
IIB	a	89.8	6.6	7.5	10.5	20.3	54.9	71.0
	b	75.0	9.1	11.1	13.7	22.5	63.8	79.9
	c	53.6	6.8	10.0	10.5	15.3	55.8	60.3
IIC	a	89.7	4.8	8.2	10.1	12.3	32.3	54.7
	b	59.2	7.6	12.5	12.3	13.8	67.8	78.0
III	a	89.3	11.9	17.4	84.1	28.8	59.8	69.1
	b	85.2	12.9	18.8	31.5	38.8	65.5	76.8
	c	77.3	15.9	26.9	33.3	71.8	158.8	179.8
	d	63.5	10.5	15.0	16.5	27.2	50.4	82.4
	e	42.6	6.5	7.8	8.9	12.5	36.4	48.6
IV	a	87.8	11.8	20.0	26.6	32.5	43.4	44.4
	b	83.1	12.7	22.4	27.3	39.3	44.6	56.1
	c	69.9	13.9	26.6	33.3	40.5	58.8	77.0
	d	39.7	5.9	16.4	21.9	38.0	53.3	59.8
V	a	89.95	6.6	10.4	18.5	25.4	38.1	59.9
	b	87.2	9.9	16.9	31.0	43.9	60.0	62.4
	c	76.6	12.3	20.5	34.1	44.8	68.1	79.4
	d	48.2	12.2	14.7	16.0	24.7	59.2	69.8

The gels in every case were allowed to stand for three days and then filtered through a muslin cloth and allowed to mature in a stone vessel in layers 5 cm thick. Samples were drawn from these at different stages of drying. These samples were washed with water in the case of Nos. 1 and 2, and the others with dilute HCl, to remove salts and metallic ions. In the case of acid washings the silica was finally washed with water. The samples were then dried in an oven for six hours at about 150° and then activated for about

two hours at 200°C in an atmosphere of CO_2. The moisture absorption at various humidities of these samples was then determined. The results are given in Table 111.

They indicate that there are large variations in the absorptive power of silica, depending on the method of preparation and the stage to which it was dried before curing. In sample No. 1 there is a gradual decrease in the absorptive capacity as the sample is matured at lower and lower moisture content. In all other cases there seems to be an optimum somewhere between 70 and 80% moisture. The enormous increase in the absorptive capacity, especially at higher humidities in the case of sample IIIC is remarkable. It is not possible to offer any explanation of this abnormality. It was noticed that water was actually flowing in this sample at higher humidities. It was not a case of swelling of the gel, but somehow free water appeared on the surface. At first it was suspected that perhaps some free acid had got on the sample, but on re-washing, drying, and activating the same phenomenon was noticed. As a general rule it appears that maturing below 60% moisture definitely results in lowering the absorptive capacity.

To study the effect of drying at higher temperature, Holmes' silica was dried over a water bath at 50 to 60%. Samples were drawn at different time intervals and moisture content determined. The samples were then washed with HCl, dried and activated as usual. Moisture adsorption with these samples was determined at different humidities. The results showed the same general run as before, when the samples were dried at ordinary temperature. There still seemed to be an optimum moisture absorption at the curing moisture content of about 70%. In Holmes' silica No. IIIC in the previous case, the enormous increase in moisture absorption mentioned in case of room temperature was not confirmed at higher temperature, for neither at 80.3% nor at 70.3% was there any phenomenal change in moisture adsorption. Of course, the results in case of sample IIIC refer to curing moisture content of 77.3%, but it should be considered near enough to 80.3%, unless this sudden increase is extraordinarily sensitive to small variations in moisture during curing.

The importance of stage of drying and curing led to trial of drying under vacuum and without vacuum over sulphuric acid. The gels were allowed to dry over sulphuric acid alone at first, and then also under vacuum so that the drying would be quicker. The samples were withdrawn, washed with water in the case of Patrick's silica and with HCl in the case of Holmes', dried and activated as usual. The moisture absorption of these samples was determined at various humidities and the results again revealed the enormous effect of drying on the moisture absorption capacity of silica. The abnormal effect of drying Holmes' silica No. III to a particular moisture content, namely, in the neighborhood of 74 per cent, was confirmed. It was noted that when the state of drying was reduced by

only 2% the moisture absorption at 90% humidity fell from 97.7 to 52.4%.

Effect of Temperature of Precipitation on Moisture Absorption

In order to study the effect of temperature at the time of precipitation of silica, Holmes' silica was prepared by mixing ferric chloride solution and sodium silicate at different temperatures. After precipitation, the gel was filtered through cloth and washed immediately with dilute acid and then with water. The sample was dried at 150°C for six hours and then activated as usual (Table 112).

It will be seen that the temperature of precipitation has an appreciable effect on moisture absorption capacity. It appears that there is an optimum at 40°C. There appears to be, however, a wide range of temperature, as the results at 23.5°C are not very different from those at 40°C or even at 60°C, though there is definite falling off at

TABLE 112. Effect of temperature of precipitation on moisture absorption by Holmes' silica.

Temperature (°C)	% Moisture at various humidities					
	10%	30%	50%	70%	90%	98%
10.0	12.3	14.4	21.5	30.7	42.5	46.9
23.5	13.8	16.6	25.9	30.9	66.4	72.8
40.0	14.2	17.1	26.9	36.7	68.8	79.9
50.0	14.1	19.2	25.9	36.0	65.3	80.0
60.0	14.5	18.5	26.0	36.4	66.3	78.9
70.0	12.7	15.7	22.4	32.1	57.4	67.2
75.0	12.6	15.8	21.5	33.8	50.8	56.1

10°C and 75°C. The optimum range of temperature may, therefore, be regarded as between 20 and 60°C.

Effect of Gradual Removal of the Metallic Ion by Acid Treatment of Silica Precipitated by the Addition of Salts of Different Metals

The well known method of preparing Holmes' silica is based on the principle that when a metallic ion is coprecipitated with silica and subsequently removed, the resulting silica is left more porous on account of the spaces which were occupied by the metallic ions. It follows from this that the size of these capillary spaces might be influenced by the atomic volume of the metallic ions. The following metallic ions were, therefore, used for coprecipitation: Fe, Cr, Al, Co, Ni, Cu, Ca, Ba, Al. The outline of the method followed in each case is given below:

Method of Preparation

I. Iron Silicate: 2 1/2 liters of 2N ferric chloride solution added to 12 1/2 liters of sodium silicate solution of density 1.032.

II. Chromium Silicate: 3 liters of 0.22N chromium chloride solution added to 3 liters of sodium silicate solution of density 1.032.

III. Cobalt Silicate: 3 liters of normal cobalt acetate solution added to 3 liters of sodium silicate solution of density 1.032.

IV. Nickel Silicate: 3 liters of normal nickel sulphate solution added to 3 liters of sodium silicate solution of density 1.032.

V. Copper Silicate: 3 liters of 0.22N copper sulphate solution with 3 liters of sodium silicate solution of density 1.032.

VI. Calcium Silicate: 3 liters of 0.22N calcium chloride solution added to 3 liters of sodium silicate solution of density 1.032.

VII. Barium Silicate: 3 liters of 0.22N barium chloride solution added to 3 liters of sodium silicate solution of density 1.032.

VIII. Aluminum Silicate: 3 liters of 0.22N aluminum sulphate added to 3 liters of sodium silicate solution of density 1.032.

The various silicates thus prepared were allowed to dry in air to a moisture content of 70 to 75%, which is found to be the optimum for maximum activity (see Table 111). The samples thus dried were treated with varying amounts of acid to remove the metallic ions to different degrees. The samples were then washed free of acid, dried and activated. The amount of metallic ion in each case was determined on the dried sample. The following properties of these samples of silica were determined:

TABLE 113. Moisture absorption of various silicates at different humidities.

Sample No.	% of metallic oxide	Humidity 10%	30%	50%	70%	90%	98%
Iron silicate matured at 74.5%							
1	9.3	5.8	7.3	8.5	11.4	21.3	42.2
2	7.73	8.6	12.0	10.0	15.7	65.8	88.3
3	5.62	7.7	13.1	18.2	21.2	51.8	84.8
4	4.11	11.9	13.6	12.6	25.3	43.5	79.2
5	2.79	10.4	14.8	14.9	22.6	63.0	79.7
6	2.19	-	-	-	18.6	64.6	71.8
7	1.15	10.9	11.9	21.1	19.5	59.9	92.2
8	0	9.5	10.9	13.7	18.8	54.2	88.0
Aluminum silicate matured at 73.7% moisture content							
1	10.42	3.1	7.2	8.4	10.3	20.2	35.1
2	7.83	5.8	8.7	9.7	16.9	35.5	55.0
3	5.16	5.2	7.7	9.5	16.2	34.8	51.3
4	3.24	8.9	10.8	12.9	18.2	37.1	63.0
5	1.75	5.8	7.6	9.6	14.4	32.2	49.9
6	0	9.8	12.5	14.2	19.1	39.5	79.9

(1) Moisture absorption at different humidities.
(2) Alcohol absorption at different relative vapor pressures.
(3) Heat of wetting.
(4) Ammonia adsorption.

(1) Moisture absorption at different humidities. The moisture absorption was studied from atmospheres of different humidities

obtained by H_2SO_4 - water mixtures of different concentrations in desiccators. Equilibrium was attained in seven days. The results are given in Table 113, only for Al and Fe silicates. The general run of the results in the case of other silicates was similar. The following general conclusions emerge from the entire data.

(1) There is gradual increase in the absorptive capacity as the metallic ion is removed.

(2) In some cases there seems to be an optimum beyond which, if the metallic ion is removed, the absorptive capacity tends to fall.

(3) Ni, Cu, Ba, on the whole show lower absorptive capacity when they are removed from their corresponding silicates than do silicates of Al, Cr, Co, Fe.

(2) Alcohol absorption. Very little work has been done on the absorption of organic vapors by silica gels. The problem is of interest from the point of view of the capillary structure of silica gel. If the absorption of vapors is entirely due to capillary condensation brought about by purely surface-tension effects, then alcohol adsorption should run parallel to moisture absorption results. The absorption of alcohol was studied by placing about 0.5 gram of the sample in desiccators containing alcohol - glycerin mixtures in the following ratio:

% by volume of glycerin in alcohol	% Relative vapor pressure
23.9	91.2
55.7	76.31
83.4	46.56
91.9	24.14

The time of exposure was seven days. The results are recorded in Table 114, for silicates of Al and Fe only. The results for alcohol absorption are parallel to those of moisture absorption.

(3) Heat of wetting. Heat of wetting was determined in a Thermos flask by adding a known weight of the sample to 200 cc of water and noting the rise of temperature. The usual precautions were observed and heat of wetting calculated in calories per 100 grams of the sample. The results of different samples are given in Table 115, the silicates of Al and Fe being selected as typical of the entire series.

(4) Ammonia absorption. 4 grams of the sample were placed in contact with 20 cc of normal ammonia and shaken in a mechanical shaker for 48 hours. Samples were then completely dried in an oven at 100 to 120°C. The dried sample was distilled with lime to drive off the ammonia, which was absorbed in standard acid and back-titrated. The amount of ammonia absorbed in milliequivalents per 100 grams of sample are included in Table 115.

TABLE 114. Alcohol absorption by various silicates.

Sample No.	% of metallic oxide	% alcohol absorbed at relative vapor pressure 21.14%	46.56%	76.31%	91.2%
Ferric silicate matured at 74.5% moisture content					
1	9.3	2.3	3.8	3.9	6.0
2	2.73	8.11	10.0	9.1	30.3
3	5.62	8.5	8.9	12.1	34.2
4	4.11	13.5	14.9	22.1	42.3
5	2.79	12.5	15.1	19.9	46.2
6	2.19	2.0	4.2	6.1	22.5
7	1.15	12.5	13.9	19.4	46.2
8	0	10.0	12.8	16.8	43.7
Aluminum silicate matured at 73.7% moisture content					
1	10.42	4.6	5.1	5.2	6.8
2	7.83	7.5	8.7	9.8	19.4
3	5.16	2.7	4.3	9.2	10.9
4	3.24	8.3	8.7	15.1	22.1
5	1.75	7.9	8.8	10.0	19.3
6	0	8.6	10.7	15.1	23.4

TABLE 115. Heat of wetting and ammonia absorption of various silicates.

Sample No.	% of metallic oxide	Heat of wetting (calories per 100 g of sample)	Ammonia taken up (m.e./100 g)
Ferric silicate matured at 74.5% moisture content			
1	9.3	16.10	46.87
2	7.73	17.37	45.0
3	5.62	23.93	43.75
4	4.11	24.44	38.75
5	2.79	22.50	36.25
6	2.19	21.45	28.75
7	1.15	22.79	27.50
8	0	22.06	20.0
Aluminum silicate matured at 73.7% moisture content			
1	10.42	14.1	40.0
2	7.83	19.5	54.37
3	5.16	15.6	56.25
4	3.24	22.2	65.0
5	1.75	19.9	62.5
6	0	25.4	42.5

It will be seen from Table 115 that there is no correlation between heat of wetting and ammonia absorption. This is easily understood when it is remembered that moisture absorption is due to capillary condensation, a purely physical phenomenon, whereas ammonia absorption is a chemical reaction between an acid and a base. However, there is some parallelism between heat of wetting and moisture absorption, as would be expected.

Effect of the Nature of Acid on the Properties of Precipitated Silica

In order to study the effect of the nature of the acid used for precipitation on the moisture absorption, heat of wetting and ammonia absorption of the precipitated silica, the following acids were used for precipitation:

I	HCl	(a ((b
II	HNO_3	(a ((b
III	H_2SO_4	(a ((b
IV	H_3PO_4	(a ((b
V	CH_3COOH	(a ((b

All acids of normality 2.74 were mixed with equal volumes of sodium silicate solution of density 1.185. The precipitated silica was filtered immediately and washed with water after seven days in one case (to get sample a) and three weeks in the other (to get sample b). The washed samples were dried and activated at 200°C in a current of CO_2 as usual. The results of moisture absorption, ammonia neutralization and heat of wetting are given in Table 116.

It will be seen that there are large variations in moisture absorption, heat of wetting, and ammonia absorption due to the nature of the acid used for precipitation. On the whole, strong acids like HCl and HNO_3 give more absorbent silica than others. It was concluded from this that perhaps pH value may be playing an important role in determining the activity of the precipitated silica. To determine the effect of pH at the time of precipitation of silica, different sam-

ples were obtained by mixing different volumes of 2.75N HCl with a fixed amount of sodium silicate solution; 150, 225, 300, 400 and 500

TABLE 116A. Moisture absorption of silica precipitated by various acids.

Sample No.	Matured at moisture (%)	% Moisture absorbed at different humidities					
		10%	30%	50%	70%	90%	98%
I a	68.6	5.4	8.2	19.8	20.7	36.3	67.1
b	49.9	6.2	8.5	16.7	19.7	29.1	46.8
II a	69.78	4.0	13.4	16.9	26.7	40.0	69.3
b	49.7	3.10	9.4	9.8	23.8	34.1	66.0
III a	68.6	1.3	7.1	8.6	10.0	23.8	80.2
b	52.3	2.0	5.1	6.1	8.9	21.5	53.1
IV a	69.6	1.1	5.5	5.3	12.1	50.6	83.1
b	49.4	3.5	5.9	8.0	12.1	39.7	85.4
V a	64.1	1.6	6.8	7.9	21.3	28.1	38.2
b	51.2	1.4	7.2	7.8	14.7	20.4	32.5

TABLE 116B. Heat of wetting and ammonia neutralization by silica precipitated with different acids.

Sample No.	Heat of wetting (calories per 100 g)	Ammonia taken up (m.e. per 100 g)
I a	20.9	7.5
b	15.4	6.25
II a	18.5	11.25
b	15.3	6.25
III a	13.0	11.25
b	17.3	7.5
IV a	10.7	6.25
b	13.5	8.75
V a	12.7	5.0
b	11.1	5.0

TABLE 117. Moisture absorption by silica samples precipitated at different pH values.

Sample No.	pH	% Moisture absorbed at different humidities					
		10%	30%	50%	70%	90%	98%
1	11.9	6.3	7.8	11.2	19.7	38.3	69.3
2	11.63	6.3	7.5	12.1	20.6	39.7	71.2
3	10.36	6.1	7.1	11.2	21.3	39.9	71.2
4	9.90	6.5	7.8	10.2	20.9	38.8	67.5
5	4.72	10.6	13.5	17.1	29.5	52.1	82.3

cc of acid were added. The pH of these solutions was then determined. The five samples thus obtained were filtered, washed, dried

and activated as usual. The moisture absorption of these samples was then determined (Table 117).

These data show that in the alkaline range there is not much difference in activity due to pH changes. There is, however, a big difference when the precipitation is done in the acidic range. This confirms the earlier results that stronger acids on the whole give more absorbent silica.

Effect of Precipitation of Silica with Ferrous and Ferric Sulphates and Subsequent Removal of Iron

As stated before, Holmes' method of preparing silica consists in precipitating iron silicate, which is then treated with acid to remove the metal. The precipitation is usually done by adding ferric chloride. To see whether the valency of the metallic ion has some influence on the properties of the resulting silica, both ferrous and ferric salts were used for precipitation; 2N solutions of ferrous and ferric sulphate were mixed with four times their volume of sodium silicate solution of density 1.032, and the gel allowed to dry in air. One sample of the iron silicate precipitated with ferrous sulphate was kept in air to dry and also to be oxidized, while another portion was allowed to dry in a stoppered bottle to prevent oxidation. The color of the ferrous silicate was blue, which subsequently changed to brown on oxidation in air. The sample kept in the stoppered bottle showed less browning at the surface, the entire mass remaining blue. The various samples after maturing were treated with acid, and then washed with water, dried and activated as before. Moisture absorption, heat of wetting and ammonia absorption of these samples were determined. The results showed that there is not much difference in the absorption power of silica prepared by using ferrous or ferric ions.

Effect of Precipitation of Silica in the Presence of Inert Substances on its Properties

As the absorptive properties of silica are mainly due to the size of the microcapillaries, it appeared reasonable to suppose that if at the time of precipitation some inert substances with high molecular weight were present, the size of the capillaries in the precipitated silica might be affected. To study this point, silica was precipitated in the presence of glycerol and sugar of different concentrations. To 500 cc of sodium silicate solution of density 1.15, containing 10, 25, 50, 87.5, 125, 250 cc of glycerin, were added 500 cc of 2.75N HCl each time. The resulting gels were washed with water till free from extraneous matter and then dried and activated as usual. The samples are named as follows:

Sample No.	Obtained by addition of the following grams of sugar to 500 cc of sodium silicate
1	10.0
2	25.0
3	50.0
4	87 1/2
5	125.0
6	175.0

Sample No.	Obtained by addition of the following cc of glycerin to 500 cc of sodium silicate
7	25
8	50
9	87 1/2
10	150
11	250

Moisture absorption, alcohol absorption, heat of wetting and ammonia absorption of these samples were determined. A close perusal of the results of precipitation in the presence of sugar or glycerin showed large variations in the properties of silica, but these variations are not in any definite order.

To increase the size of the capillaries, Al and Fe silicates were precipitated in the presence of excess of Al_2O_3 and Fe_2O_3. The experiment was arranged as follows:

Excess NaOH was added to sodium silicate, to which Fe or Al salts were then added, thus precipitating an excess of the hydroxide with the silicate. Fe and Al were then gradually removed from the precipitated gels and the following fractions were obtained:

(1) Sample of ferric silicate. 4 liters of sodium silicate solution of density 1.032 were mixed with 4 liters of NaOH solution and to this 8 liters of 2N ferric chloride were added. The gel was filtered after 3 to 4 days and allowed to mature in atmosphere. After nearly a week, the entire quantity was divided into six parts and to these increasing amounts of the acid were added. The samples were washed, dried and activated and the per cent of Fe_2O_3 determined in each.

Sample No.	% of Fe_2O_3
1	36.2
2	26.45
3	22.4
4	12.9
5	5.8
6	0

(2) Samples of Al silicate. 4 liters of sodium silicate solution of density 1.032 were mixed with 4 liters of normal sodium hydroxide solution and to this 8 liters of 0.22N aluminum sulphate were added. The resulting gel was filtered and allowed to mature in air and then treated with varying amounts of acids, washed, dried and activated as usual. The per cent of Al_2O_3 was determined in each sample.

Sample No.	% of Al_2O_3
7	22.0
8	17.14
9	13.50
10	8.99
11	5.81
12	0

(3) Samples of ferroalumino silicate. 5 liters of sodium silicate solution of density 1.032 were mixed with 5 liters of normal NaOH and to this were added 6 liters of nearly normal solution with respect to both Al sulphate and ferric chloride. The gel was allowed to stand for a couple of days, allowed to mature in air for six days, and then treated with different amounts of acid. The per cent of sexquioxides was then determined in each case.

Sample No.	% Fe_2O_3	% Al_2O_3
13	17.46	7.99
14	15.18	6.47
15	12.50	5.12
16	8.98	3.82
17	2.60	2.39
18	0	0

Moisture absorption results are given in Table 118. The results of this study, coupled with previous observations, give rise to the general conclusion that the precipitation of silica and the nature of its capillary structure are largely dependent on chance association of a number of factors. This points strongly to the fact that moisture absorption by silica is mainly a physical effect which depends on the size distribution of minute capillaries. The formation of these capillaries is capable of infinite variations, and the properties of resulting silicas as regards moisture absorption must vary correspondingly. It is significant to note that if the variations were entirely due to differences in the extent of the surface, the vapor

pressure curves would shift bodily one way or the other. On the other hand, if a change occurs in the size distribution of capillaries, the resulting silica will show unequal changes in moisture absorption at all humidities. The moisture absorption of silica, therefore, is entirely due to capillary condensation at all humidities.

TABLE 118. Moisture absorption by silica samples precipitated in excess of Fe_2O_3 and Al_2O_3.

Sample No.	% Moisture absorbed at different humidities					
	10%	30%	50%	70%	90%	98%
1	4.1	6.9	8.8	12.6	24.7	50.7
2	5.9	9.5	10.6	18.7	34.3	66.3
3	7.8	12.8	16.8	26.3	59.9	97.2
4	6.3	11.0	15.9	21.5	34.9	52.7
5	9.8	14.6	16.1	22.1	39.2	70.6
6	10.0	15.1	16.0	24.1	44.6	77.5
7	1.4	4.0	4.2	6.6	14.8	37.1
8	3.5	3.6	4.3	8.9	20.7	42.5
9	5.6	7.8	10.5	13.9	24.6	49.5
10	5.7	14.8	15.1	19.6	29.5	58.0
11	4.7	9.8	10.7	16.3	27.7	55.6
12	5.8	10.6	11.2	14.5	27.3	57.1
13	8.1	13.1	16.0	29.1	57.1	117.5
14	5.4	7.1	12.2	21.1	40.0	75.6
15	4.8	6.8	8.7	14.4	30.0	56.5
16	3.9	7.0	7.3	15.1	37.1	84.2
17	2.3	4.5	5.3	9.8	20.1	52.2
18	1.3	3.3	3.9	5.5	13.8	39.7

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